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B.Com Sem II (CBCS)

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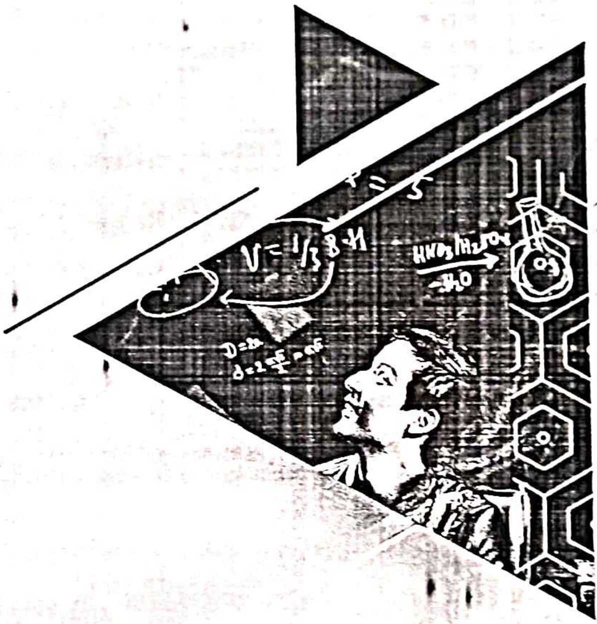

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J.B.S. Publishers Faridabad (HRY)

Published By:

J.B.S. Publishers and Distributors

jbspublisherfbd@gmail.com

(Mohit Communication Shop No. 16, Rama Dairy Market Sect-3 Faridabad)

Text to read free is available on the site jbspublishers.com

Phone : 9467361123, 9868725603, 8010133360.

ISBN 978-93-84009-18-2

Edition 2022

Price ₹ 230/-

BUSINESS MATHEMATICS

B.Com Sem-I

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J.B.S. Publishers and Distributors

Mohit Communications, shop No. 16, Rama dairy market Sector-3, Ballabgarh.(09716668074)

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Phone : 08527187130, 9868725603.
e-mail : jbspublisherfbd@gmail.com

1st Edition 2010
IInd Edition 2011
IIIrd Edition 2012
IVth Edition 2013
VIIIth Edition 2016
Revised Edition 2019

Price ₹ 230/-

ISBN-978-93-84009-23-6

CHAPTE
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Role of State and Market :

In The Context of Indian Higher Education Sector

Edited By

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Alankar Publishing House

Delhi

Role of State and Market :

In The Context of Indian Higher Education Sector

First Edition : 2021

ISBN : 978-93-86817-49-5
Price : 595.00

Published by

Alankar Publishing House

1/9929, West Gorakh Park
Gali No. 3H, Shahdara, Delhi-110032
Mobile : 9810429755 / 9999163460
E-mail : alankar_books07@yahoo.com

Branch :

H.No.11, Bhaikhunthpur, Lalmati
Guwahati-781029 (Assam)

Printed in India by Abhishek Tondon for **Alankar Publishing House**

Content

Preface (v-vii)

Chapter- 1 State vs. Market : In the Context of Higher Education
Jyoti Atri 11

Chapter- 2 Privatization of Higher Education in India
Jyoti Atri 29

Chapter- 3 An Evaluation of New Education Policy in Context of Higher Education
Suman Rani 55

Chapter- 4 New Education Policy- A New Dawn
Anayatullah Nayaji 69

Chapter-5 New Education Policy and Challenges of Rural Students
Dr. Joginder Singh & Dr. Pramjeet Singh 81

Chapter-6 Globalization and Higher Education in India
Sanjeev Kumar 89

Chapter-7 Emerging Social & Economic Issues Due to Privatization of Higher Education in India
Jyoti Atri 109

The crystal structure, refinement and dielectric properties of Ba and Mn substituted bismuth ferrite

Cite as: AIP Conference Proceedings 2142, 040027 (2019); https://doi.org/10.1063/1.5122364
Published Online: 29 August 2019

Manisha Rangi, Sujata Sanghi, Ashish Agarwal, Sandhaya Jangra, and Jogender Sangwan

The Crystal Structure, Refinement and Dielectric Properties of Ba and Mn Substituted Bismuth Ferrite

Manisha Rangi[1,a)], Sujata Sanghi[2,b)], Ashish Agarwal[2,c)], and Sandhaya Jangra[2,d)], Jogender Sangwan[2,e)]

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Abstract. The effect of Ba and Mnsubstitution on the crystal structure and dielectric properties of $BiFeO_3$ has been studied using X-ray diffraction at room temperature, Rietveld refinement and dielectric properties measurements technique. Single phase $Bi_{0.8}Ba_{0.2}Fe_{1-x}Mn_xO_3$ (x= 0.01, 0.05)multiferroics have been synthesized by two stage solid state reaction method. Rietveld refinement of both the samples revealed thatthe synthesized ceramics exhibit rhombohedral structure with space group R3c as of parent $BiFeO_3$.The dielectric response of both samples was analyzed in the frequency range 100 Hz–2 MHz at different temperatures revealing dispersion in dielectric constant (ε′) and in dielectric loss (tanδ) at lower frequencies. Both ε′ and tan δ increase with increase of Mn content.

INTRODUCTION

Now a day, there has been revival of interest in multiferroics materials in which magnetism and ferroelectricity exists in single phase. Such materials are relatively rare and interesting due to the physics behind them [1, 2]. Among all multiferroic materials, Bismuth Ferrite has gain so much attention as it is the only known material which has ferroelectric and antiferromagnetic orders (ferroelectric Curie temperature $T_C \sim$ 1100K and high antiferromagnetic Neel temperature $T_N \sim$ 640K) well above room temperature. This behavior makes it suitable for various practical applications like sensors, actuators, memory devices etc.$BiFeO_3$ (BFO) has a rhombohedrally distorted perovskite structure with space group R3c in which polar cation (Bi^{3+}) is present at A-site and magnetic cation (Fe^{3+}) at B-site with G-type antiferromagnetic order [3-4]. Apart from the positives BFO has some problems as well which are (i) it has spiral spin structure which inhibits the macroscopic magnetization (ii) synthesis of single phase BFO (iii) high leakage current and low electrical resistivity [3-5].Many solutions have been tried up and among them ionic substitution is found to be suitable to minimize these issues. So in this present work, substitution of diamagnetic divalent ion i.e., Ba is done at Bi site and transition metal ion i.e., Mn at Fe site is done and there structural and dielectric properties has been studied.

EXPERIMENTAL DETAILS

Conventional two stage solid state reaction method has been employed to synthesize the $Bi_{0.8}Ba_{0.2}Fe_{1-x}Mn_xO_3$(x=0.01, 0.05).The appropriate materials Bi_2O_3, $BaCO_3$, Fe_2O_3, and Mn_2O_3, (≥99% pure) reagents were taken in stoichiometric ratio, mixed properly and grounded in an agate mortar to obtain a homogenous mixture. These mixtures were calcined at673 K for 4h at the rate of 5 K /minand grinding was again done for 1hour to get

Advances in Basic Science (ICABS 2019)
AIP Conf. Proc. 2142, 040027-1–040027-4; https://doi.org/10.1063/1.5122364
Published by AIP Publishing. 978-0-7354-1885-1/$30.00

more homogeneous mixture. Final sintering was carried out at 1123 K for 4 hours for and cooled at room temperature to obtain a single phase perovskite. Structural Characterization was done by X-ray diffraction at room temperature. XRD patterns were collected by using RigakuMiniflex-II diffractometer with CuK_α radiation (λ = 1.54Å) in the 2θ range from 20° to 80° with the scanning rate of 2° min^{-1} at room temperature. Rietveld Refinement of XRD data has been carried out using FullProf program. The impedance measurement was performed using an impedance/gain phase analyzer (Newton's 4th Ltd.). Dielectric data was recorded in the frequency range of 100 Hz to 1 MHz and temperature range 313 K to 623 K.

RESULT AND DISCUSSION

XRD pattern of polycrystalline $Bi_{0.8}Ba_{0.2}Fe_{1-x}Mn_xO_3$ (x=0.01, and 0.05 and henceforth designated as Mn 01 and Mn 05 respectively) multiferroics (Figure 1) exhibit single phase perovskite structure with traces of impurity phases ($Bi_2Fe_4O_9$, $Bi_{25}FeO_{39}$). Absence of any extra peak in both the sample indicates that no complete structural transformation takes place.

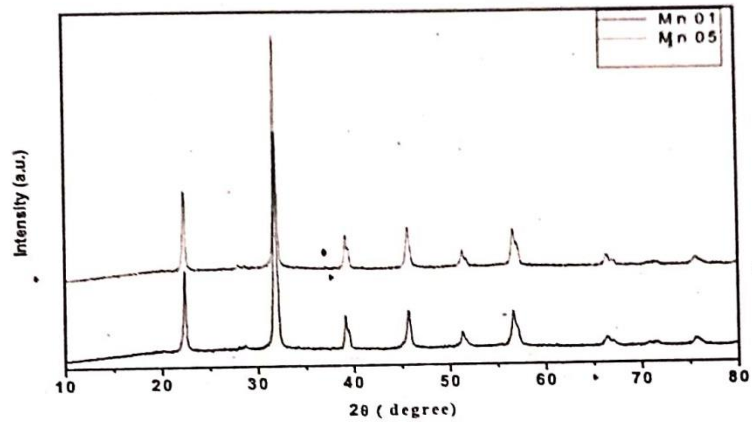
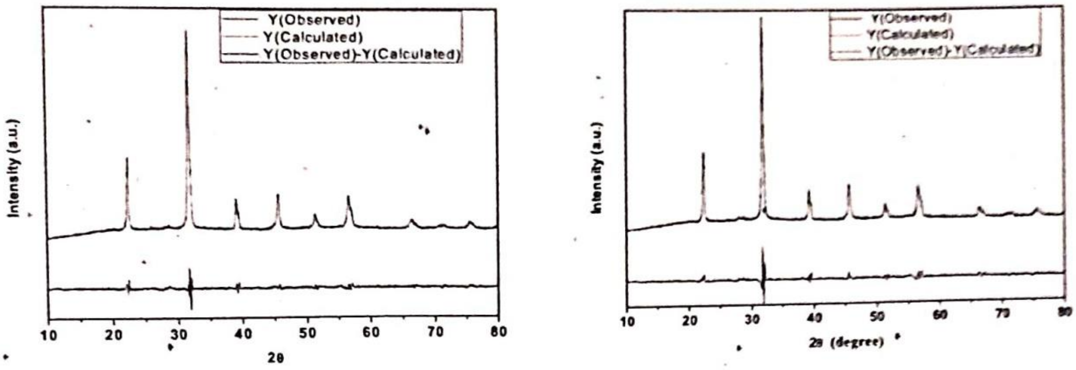


FIGURE 1.XRD patterns of $Bi_{0.8}Ba_{0.2}Fe_{1-x}Mn_xO_3$ (x = 0.01, and 0.05) multiferroic samples at room temperature.

In order to analyse the structural properties, the observed XRD patterns of both the samples have been refined using the Rietveld refinement method by FullProf program. Structure of $Bi_{0.8}Ba_{0.2}FeO_3$ has been ascribed to rhombohedral with space group R3c as reported earlier [4]. The ground state space group does not change with Mn substitution which is also reported by Yin et al [6]. Therefore Rietveld refinement of Mn01, Mn 05 samples was performed using same space group i.e. R3c and the structural model allow us to reproduce all the observed peaks. The observed, simulated and difference XRD pattern resulting from refinement are shown in Figure 2.



(a) (b)

Figure 2. Observed, calculated and difference of Rietveld refined XRD patterns of $Bi_{0.8}Ba_{0.2}Fe_{1-x}Mn_xO_3$ (a) x = 0.01, (b) x = 0.05 samples.

The refined parameters are listed in table 1. With increase in the content of Mn, lattice parameters '*a*', '*c*' and volume decreased.But ionic radii of Mn^{3+} are same as that of Fe^{3+} i.e. 0.645 Å, which normally suggests that there should be no change in the lattice parameters with increase in the manganese content. But Fe and Mn are versatile species with multiple oxidation state,which points towards that Mn exists in Mn^{4+}state as also reported earlier [7].

TABLE 1. Refined structural parameters of $Bi_{0.8}Ba_{0.2}Fe_{1-x}Mn_xO_3$ samples only.

Concentration	**Mn=0.01**	**Mn=0.05**
Crystal Structure	Rhombhohedral	Rhombhohedral
Lattice paramters	a =5.6359Å c =13.6926Å V =376.661Å^3	a =5.6314Å c =13.6905Å V =376.457Å^3
Atomic Positions	Bi/Ba(0, 0, 0.2361) Fe/Mn (0, 0, 0) O (0.8018, 0.6270, 0.4288)	Bi/Ba(0, 0, 0.2391) Fe/Mn (0, 0, 0) O (0.7912, 0.6053, 0.4304)
R-factors	R_p = 4.14 R_{wp} = 5.38 χ^2 = 3.49	R_p = 4.81 R_{wp} = 6.43 χ^2 = 4.91

Figure 3 represents the frequency dependence response of dielectric constant (ε') and dielectric loss (tan δ) for all the ceramics at different temperature. The dielectric constant for all the samples shows dispersion behaviour at low frequencies, and becomes constant at higher frequencies. Large values of ε' at low frequencies may be ascribed to the interfacial dislocations, oxygen vacancies, grain boundary effect etc., while as frequency is increased the charge carriers are not able to follow the applied external applied field and so there is a decrease in dielectric constant. This type of behaviour may be explained on the basis of Maxwell Wagner type interfacial polarization [8-9]. According to M-W model, the dielectric material is made up of well conducting layer of grains that are separated by grain boundaries which are highly resistive. At low frequency, grain boundaries have more impact than the grains and due to this charge accumulate near the boundary causes high dielectric constant. Howsoever at high frequency grains comes into play which in turn reduced the probability of hoping conduction mechanism, results in the decrement in dielectric constant in that region and become constant at high frequency regime [10]. Similar behavior was observed in dielectric loss. At low frequency,grain boundary offered high resistance leads to large energy dissipation and high value of dielectric loss. On the contrary, at high frequency low resistance is offered by grains, causes small value of dielectric loss[8-10].

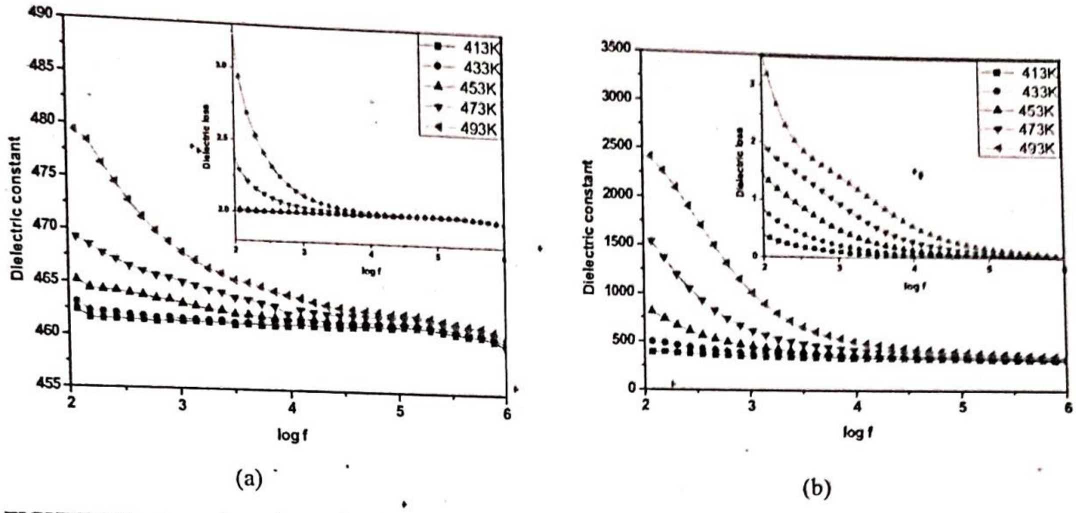


FIGURE 3. Frequency dependence of real part of dielectric constant (ε') and dielectric loss (tan δ) at inset of $Bi_{0.8}Ba_{0.2}Fe_{1-x}Mn_xO_3$ for (a) x = 0.01, (b) x = 0.05.

As the temperature increases, dielectric constant also increases due to the thermal conduction hopping mechanism. With increase in concentration of Mn dielectric constant increase appreciably which is the desirable result.Improvement in dielectric properties may be attributed to the suppression of oxygen vacancies created by the substitution of divalent ion (Ba^{2+}) in place of volatile trivalent ion (Bi^{3+}) by high valance of Mn ion to neutralise the charge [10, 11].

CONCLUSIONS

$Bi_{0.8}Ba_{0.2}Fe_{1-x}Mn_xO_3$(x=0.01, 0.05) multiferroics were synthesized by solid state reaction method. XRD pattern and Rietveld refinement shows that all the samples are phase pure and crystallized in rhombohedral structure with space group R3c. Dispersive behavior of dielectric constant (ε') anddielectric loss (tan δ) is observed at low frequency. Improved dielectric properties are attributed to the suppression of oxygen vacancies by Mn ion.

ACKNOWLEDGMENTS

Authors are thankful to DST, New Delhi (FISTScheme) for providing XRD facilities

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AIP Conference Proceedings

Structural, dielectric and magnetic properties of (Ho, Ti) modified BFO

Cite as: AIP Conference Proceedings **2142**, 040028 (2019); https://doi.org/10.1063/1.5122365
Published Online: 29 August 2019

Jogender Singh, Ashish Agarwal, Sujata Sanghi, Manisha Rangi, Tanvi Bhasin, and Sandhaya Jangra

Structural, Dielectric and magnetic Properties of (Ho, Ti) Modified BFO

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Abstract. $Bi_{0.80}Ho_{0.20}Fe_{0.80}Ti_{0.20}O_3$multiferroicswas synthesized by method of mixed-oxide route. The XRD,dielectric properties and magnetic measurements of the compound were carried out. The X-ray structural analysis shows mixed phase.Rietveld refinement of the XRD patterns deduce that the found it fit by the mixed phase setting of rhombohedral R3c and triclinic P1 space group. The change in crystal structure is attributed to the distortion of FeO_6 octahedra due to replacing a part of B- site Fe ions by Ti ions. Magnetic evaluation were performed at room temperature up to an external magnetic field of ±16kOeIt was observed that the Ti co-dopingshows a significant role for the improving multiferroics properties.

INTRODUCTION

The materials in which at least two of ferroelectric, ferromagnetic and ferro-elastic ordering exhibit in the same phasesimultaneously have been under concentrated study recently [1-2].These materials have greatuse in the large magneto electric effect and have potential application which include information storage, spintronic devices, sensors etc. $BiFeO_3$ (BFO) belongs to this class [3] at room temperature. It is only single phase fascinating multiferroic material because of its high ferroelectric Ctrie temperature, (T_c=1143 °K) and antiferromagnetic (AFM) Neel temperature (T_N =643K) [3-4]. The simultaneous doping of titanium and lanthanide can enhance together electrical and magnetic properties of $BiFeO_3$.Some other exciting results also have been reported in literature for $BiFeO_3$ when codoped with La and Ti;Dy and Ti[5].In this study, we have fabricated $BiFeO_3$ ceramics with codoping of Ho and Ti and found enhancement in electrical and magnetic properties.

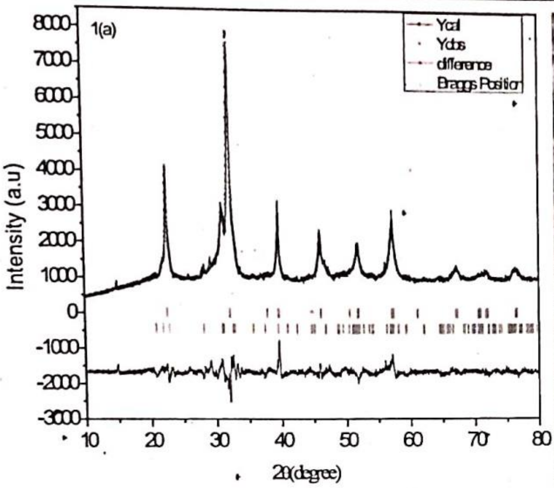
Various attempts have been made by many researchers to enhance the multiferroicscharacteristics of BFO by co-doping at the sites A and B simultaneously. As Ho possesses high magnetic moment, so Bi has been substituted with it in the present work and therefore, co-doped $BiFeO_3$ceramic samples in which doping is done by Ho at A-site and Ti at B-site.

EXPERIMENTAL DETAILS

High quality oxide powders of Bi_2O_3, Ho_2O_3 ,Ti_2O_3 and Fe_2O_3 procured from Sigma Aldrich, their particular amount in stochiometric ratio was grounded thoroughly with the help of mortar and pestle for 2 hours and then calcinated for 3 hours at 400°C. The calcinated compound then grounded for 1 hour and sintered for 1 hour at 820°C in an alumina crucible. Structural analysis were performed using X-ray diffraction (XRD) using Rigaku-Miniflex II Desktop X-Ray diffractometer, scanning electron microscopy. The quality XRD pattern was further analyzed using a Rietveld refinement and Edper program in FullProf suite software. Micrographs evaluation were carried out using JEOL scanning electron microscope (SEM), respectively. Magnetization measurements were performed at room temperature using vibrating sample magnetometer (VSM) (model Lakeshore,7304).

Advances in Basic Science (ICABS 2019)
AIP Conf. Proc. 2142, 040028-1–040028-3; https://doi.org/10.1063/1.5122365
Published by AIP Publishing. 978-0-7354-1885-1/$30.00

Sample	Model	Cell (Å)	Atom	x	y	Z	R-factor
	R3c	a= 5.5693	Bi/Ho	0.0000	0.0000	0.02485	
	(66.42%)	b= 5.5693	Fe/Ti	0.0000	0.0000	0.25115	
		c=13.6702	O	-0.1984	1.6068	0.7148	R_p=4.90
$Bi_{0.80}Ho_{0.20}Fe_{0.80}Ti0_{.20}O_3$		V= 367.204(Å^3)					
	P1	a= 4.3307	Bi/Ho	0.16159	7.85772	0.37914	R_{wp}=6.27
	(33.58%)	b= 4.0994	Fe/Ti	0.63868	8.46743	0.91230	
		c =3.8903	O1	1.5028	1.8327	0.1741	χ^2=4.88
		V= 68.2819(Å^3)	O2	2.8796	0.7321	-1.0982	
			O3	-1.2690	1.1918	5.6569	



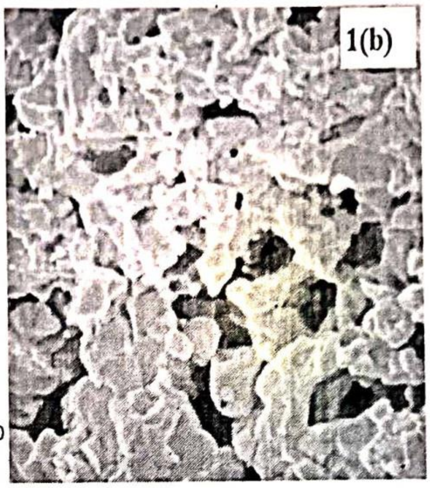


Fig 1.The Rietveld refined XRD patterns and 1(b) SEM micrographs of$Bi_{0.80}Ho_{0.20}Fe_{0.80}Ti0_{.20}O_3$ ceramic.

Fig. 1 shows the Rietveld refined XRD spectrums of $Bi_{0.80}Ho_{0.20}Fe_{0.80}Ti_{0.20}O_3$ The Rietveld refinement of XRD pattern was best fitted by the mixed phase assumption including rhombohedral R3c (≈66.42%) and triclinic P1 (≈33.58%).

The parameters obtained from refinement are summarized in Table I.

Table 1. Rietveld refined structural parameters of Bi0.80Ho0.20Fe0.80Ti0.20O3 of XRD.

Fig. 1(b) explain scanning electron micrographs (SEM) of $Bi_{0.80}Ho_{0.20}Fe_{0.80}Ti_{0.20}O_3$. The micrographs represent the dense and uniform morphology of the sample. It signifies that Ti doping suppressesthe growth of grainsresulting in small grain sizes of highly doped sample reflects in the SEM micrographs. Another possible reason of decrease in grain sizesis the dissimilarity in the ionic radius of Bi^{3+} and Ti^{3+}. Earlier studies suggested that the reduction in the grain size is ascribed to the suppression of oxygen vacancies with the Ti doping. Since the motion of oxygen vacancies during the sintering mechanismare responsible forgrowth of grains.Structural symmetry for (Ni, Co, Cd, Nd, Ho with Ti) co-doped BFO is summerized in Table 2.

TABLE 2. Structural symmetry for (Ni,Co,Cd,Nd,Ho with Ti) co-doped BFO is summerized.

S. No.	Compounds Name	XRD Structure	Average Crystallite Size	Reference
1.	$Bi(Ni_{1/4}Ti_{1/4}Fe_{1/2})O_3$	Orthorhombic Symmetry	28 nm	[2]
2.	$Bi(Ni_{0.45}Ti_{0.45}Fe_{0.10})O_3$	Tetragonal Symmetry	30 nm	[4]
3.	$Bi(Ni_{0.40}Ti_{0.40}Fe_{0.20})O_3$	Orthorhombic Symmetry	36 nm	[1]
4.	$Bi(Co_{1/4}Ti_{1/4}Fe_{1/2})O_3$	Orthorhombic Symmetry	30 nm	[3]
5.	$Bi_{0.90}Nd_{0.10}Fe_{0.93}Ti_{0.07}O_3$	Triclinic Symmetry	--	[5]
6.	$Bi_{0.80}Ho_{0.20}Fe_{0.80}Ti_{0.20}O_3$	Triclinic+ Orthorhombic Symmetry	26 nm	Present work

MAGNETIC ANALYSIS

Prestine BFO exhibiting a spatially modulated spin configuration along with G-type antiferromagnetic ordering which does not permitthe resulting net magnetization [2].On the basis of various reports it is concluded that Tico-doping at B-site of BFO is very effective in order to enhance the magnetic properties of BFO.Fig. 2 shows *M-H* hysteresis curves of the synthesised sample with a maximum field of ±10kOe at room temperature.The magnetic parameters calculated from *M-H* loop and comparison with published report are listed in Table3

TABLE 3. Comparison between magnetic paramettcrs for co-doping (Ti) BFO.

S. No.	Compounds Name	Magnetic Parameters		Reference
		M_S(emu/g)	H_C(Oe)	
1.	$Bi(Ni_{1/4}Ti_{1/4}Fe_{1/2})O_3$	0.131	298.98	[2]
2.	$Bi(Ni_{0.40}Ti_{0.40}Fe_{0.20})O_3$	0.363	389	[1]
3.	$Bi(Co_{1/4}Ti_{1/4}Fe_{1/2})O_3$	2.66	653.75	[3]
4.	$Bi_{0.80}Ho_{0.20}Fe_{0.80}Ti_{0.80}O_3$	0.144	67.77	Present work

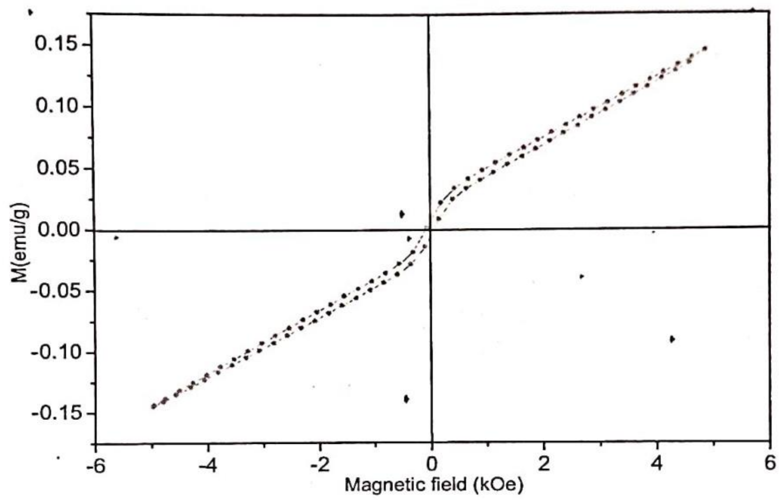


Fig 2 M-H hysteresis loop recorded at room temperature of $Bi_{0.80}Ho_{0.20}Fe_{0.80}Ti_{0.20}O_3$

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Gandhi and Global Peace
गाँधी और विश्व शांति

Editor
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ANN-III (B)

SHIVALIK PRAKASHAN
Delhi Bharat

First Edition : 2022
ISBN : 978-93-91214-21-0
Price : 1295/-

Publisher:
SHIVALIK PRAKASHAN
4648/21, Ansari Road
Delhi-110002
Phone : 011-42351161
Mob. : +91-9811693579
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Branch Office
Plot No. 394, Sanjay Nagar Colony
Pahriya, Ramdattpur, Varanasi, Uttar Pradesh

Published in India

Published by Virendra Tiwari for Shivalik Prakashan, 4648/21, Ansari Road, Delhi-110002. Type Setting Friends Graphics and Printed by R.K. Offset Printers, Delhi.

Gandhi and Global Peace
गाँधी और विश्व शांति

Editors :
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Prof. Sanjay Kumar

Contents

Preface v

1 Relating Gandhi's Focus on Decentralization and Nonviolent Peace to Issues of Nonviolence, Globalism, and Global Peace 1
Prof. Douglas Allen

2 Gandhi, Truth and Terrorism 18
Prof. Mark Juergensmeyer

3 Gandhiji's Search for the Individual's Moral Foundations 33
Prof. Gianluigi Segalerba & Kathrin Bouvot

4 Truth, God and Justice: Walking and Meditating with Gandhi 47
Prof. Ananta Kumar Giri

5 Relevance of Gandhi's Ahimsa in Modern World: Cultural Identity and Social Responsibility 58
Ram Ohei & Duanthaolin Panmei

6 Mohandas Karamchand Gandhi: From Local to Global 67
Dr. Madan Gopal Tyagi

7 How Gandhian Views on Labour are Relevant in Present Context? 72
Aninder Singh

8 Fostering Nation's Growth Through Adopting Gandhiji's Idea of Peace 82
Dr. Preeti Devi

22. नफरत से सबक — 201
डॉ. राकेश तिवारी

23. गाँधी: एक वैश्विक विचारधारा — 210
डॉ. अनिल कुमार

24. महात्मा गाँधी और विश्व शांति — 216
डॉ. साधना तोमर

25. विश्व शान्ति पर गाँधी जी के विचारों की प्रासंगिकता — 220
डॉ. जसवेन्द्र सिंह

26. स्वातंत्र्योत्तर हिन्दी नाटकों में अभिव्यक्त गाँधीवादी विचार — 226
डॉ. राजवीर वत्स

27. कलम के जरिए शांति का संदेश — 234
डॉ. अटल तिवारी

28. गाँधी जी की विकेंद्रीकरण की अवधारणा और विश्व शान्ति — 246
डॉ. सुरेंद्र सिंह

29. गाँधी का वैश्विक परिदृश्य — 254
डॉ. कुसुम लता

30. शान्तिदूत महात्मा गाँधी — 260
डॉ. मानवेश नाथ दास

31. गाँधी और उनके हरिजन समाज के उत्थान के प्रयास और कार्य: भावी समाज सुधारों के लिए एक दृष्टिकोण — 265
डॉ. अरविन्द

32. वैश्विक शान्ति के गाँधीवादी उपागम — 272
डॉ. अमित कुमार पाण्डेय

DIFFERENTIAL EQUATION WITH NUMERICAL METHODS

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ISBN- 978-93-91150-35-8

Printed and Published by:
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Table of Contents

Chapter No.	Chapter Name	Page No.
PREFACE		Iv
1	A STUDY OF FUZZY GRAPH ENERGY AND ITS APPLICATIONS Mr. Baldev	1-17
2	METHODS OF GROUP TRANSFORMATION IN THE INVESTIGATION OF SOME FLUID FLOW PROBLEMS Mr. Baldev	18-33
3	USING SPLINE COLLOCATION, A NUMERICAL STUDY OF ENGINEERING BOUNDARY VALUE PROBLEMS Mrs. Richa Rani	34-43
4	A STUDY OF GRAPHS IN CERTAIN KINDS OF DOMINANCE Mrs. Seema Duhan	44-62
5	A COMPARISON OF HERMITEGALERKIN METHODS FOR NUMERICAL SOLUTION OF SECOND ORDER BOUNDARY VALUE PROBLEMS WITH OTHER NUMERICAL METHODS Mrs. Richa Rani	63-76
6	A STUDY OF USING THE ADOMIAN DECOMPOSITION METHOD IN FRACTIONAL DIFFERENTIAL EQUATIONS OF FLOW PROBLEMS Dr. Garima Kumari	77-98
7	A STUDY OF DIMENSIONAL ANALYSIS AND DIFFERENTIAL EQUATIONS Dr. Garima Kumari	99-121
8	AN ALGEBRAIC AND GRAPH THEORETIC STUDY OF POSETS AND RELATED ASPECTS Mrs. Seema Duhan	122-139
9.	A STUDY ON GRAPHS FROM THE RING OF MATRICES Mr. Kamal	143-161
10.	APPLICATIONS OF ALGEBRAIC CONCEPTS OF HYDROCARBON IN GRAPH THEORY Mr. Kamal	162-183

< Back

Chapter in Edited Book

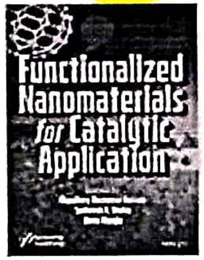
Chapter 13

Functionalized Nanomaterials for Catalytic Application: Trends and Developments

Meena Kumari, Badri Parshad, Jaibir Singh Yadav, Suresh Kumar

Book Editor(s):Chaudhery Mustansar Hussain, Sudheesh K. Shukla, Bindu Mangla

First published: 14 June 2021 | https://doi.org/10.1002/9781119809036.ch13 | Citations: 1



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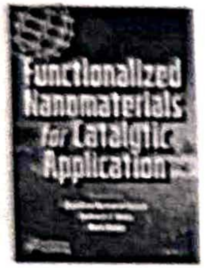
Summary

Catalysis by functionalized nanomaterials is the contemporary discipline of nanoscience which is expanding exceptionally to meet the upcoming global demands of mankind. Nanocatalysts, being lying at the frontier of homogeneous and heterogeneous catalysts, offer multiple benefits of atom economy, remarkable stability, enhanced activity, better selectivity, recoverability, reusability, and energy efficiency, thereby allowing optimum feedstock utilization and minimal chemical waste. However, with time, it was diagnosed that some of these very active nanocatalysts suffer with the limitation of stability causing them to agglomerate during catalysis, which was later resolved to a great extent by modifying their surface composition via functionalization. The functionalization of these nanocatalysts with various biocompatible and active species serving as weak ligands not only enhances their stability and selectivity but also facilitates their easy separation along with preventing their undue coagulation during catalysis. Besides these, the functionalization of nanomaterials also has considerable effect reflected in their structure, morphology, optical, electrical, magnetic, and other properties owing to the novel theory of quantum effects, enabling a control of their catalytic activity.



Functionalized Nanomaterials for Catalytic Application

Editor(s): Chaudhery Mustansar Hussain, Sudheesh K. Shukla, Bindu Mangla

First published: 14 June 2021

Print ISBN: 9781119808978 | Online ISBN: 9781119809036
| DOI: 10.1002/9781119809036

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- Table of Contents

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Front Matter (Pages: i-xviii)

Summary PDF Request permissions

CHAPTER 1

Functionalized Nanomaterial (FNM)–Based Catalytic Materials for Water Resources (Pages: 1-51)

S. Sreevidya, Kirtana Sankara Subramanian, Yokraj Katre, Ajaya Kumar Singh, Jai Singh

Summary PDF References Request permissions

CHAPTER 2

Functionalized Nanomaterial (FNM)–Based Catalytic Materials for Energy Industry (Pages: 53-88)

Amarpreet K. Bhatia, Shippi Dewangan, Ajaya K. Singh, Sónia. A.C. Carabineiro

Summary PDF References Request permissions

CHAPTER 3

Bionanotechnology-Based Nanopesticide Application in Crop Protection Systems (Pages: 89-107)

Abhisek Saha

Summary **PDF** **References** **Request permissions**

CHAPTER 4

Functionalized Nanomaterials (FNMs) for Environmental Applications (Pages: 109-134)

M.B. Bhavya, Swarnalata Swain, Prangya Bhol, Sudesh Yadav, Ali Altaee, Manav Saxena, Pramila K. Misra, Akshaya K. Samal

Summary **PDF** **References** **Request permissions**

CHAPTER 5

Synthesis of Functionalized Nanomaterial (FNM)–Based Catalytic Materials (Pages: 135-168)

Swarnalata Swain, Prangya Bhol, M.B. Bhavya, Sudesh Yadav, Ali Altaee, Manav Saxena, Pramila K. Misra, Akshaya K. Samal

Summary **PDF** **References** **Request permissions**

CHAPTER 6

Functionalized Nanomaterials for Catalytic Applications—Silica and Iron Oxide (Pages: 169-184)

Deepali Ahluwalia, Sachin Kumar, Sudhir G. Warkar, Anil Kumar

Summary **PDF** **References** **Request permissions**

CHAPTER 7

Nanotechnology for Detection and Removal of Heavy Metals From Contaminated Water (Pages: 185-226)

Neha Rani Bhagat, Arup Giri

Summary **PDF** **References** **Request permissions**

CHAPTER 8

Nanomaterials in Animal Health and Livestock Products (Pages: 227-250)

Devi Gopinath, Gauri Jairath, Gorakh Mal

Summary **PDF** **References** **Request permissions**

CHAPTER 9

Restoring Quality and Sustainability Through Functionalized Nanocatalytic Processes (Pages: 251-259)

Nitika Thakur, Bindu Mangla

Summary **PDF** **References** **Request permissions**

CHAPTER 10

Synthesis and Functionalization of Magnetic and Semiconducting Nanoparticles for Catalysis (Pages: 261-302)

Dipti Rawat, Asha Kumari, Ragini Raj Singh

Summary **PDF** **References** **Request permissions**

CHAPTER 11

Green Pathways for Palladium Nanoparticle Synthesis: Application and Future Perspectives (Pages: 303-328)

Arnab Ghosh, Rajeev V. Hegde, Sandeep Suryabhan Gholap, Siddappa A. Patil, Ramesh B. Dateer

Summary **PDF** **References** **Request permissions**

CHAPTER 12

Metal-Based Nanomaterials: A New Arena for Catalysis (Pages: 329-353)

Vats Monika, Sharma Gaurav, Varun Sharma, Varun Rawat, Kamalakanta Behera, Arvind Chhabra

Summary **PDF** **References** **Request permissions**

CHAPTER 13

Functionalized Nanomaterials for Catalytic Application: Trends and Developments (Pages: 355-415)

Meena Kumari, Badri Parshad, Jaibir Singh Yadav, Suresh Kumar

Summary **PDF** **References** **Request permissions**

CHAPTER 14

Carbon Dots: Emerging Green Nanoprobes and Their Diverse Applications (Pages: 417-492)

Shweta Agarwal, Sonika Bhatia

Summary **PDF** **References** **Request permissions**

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Index (Pages: 493-503)

First Page **PDF** | **Request permissions**

13

Functionalized Nanomaterials for Catalytic Application: Trends and Developments

Meena Kumari[1*], Badri Parshad[2], Jaibir Singh Yadav[3] and Suresh Kumar[4†]

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Abstract

Catalysis by functionalized nanomaterials is the contemporary discipline of nanoscience which is expanding exceptionally to meet the upcoming global demands of mankind. Nanocatalysts, being lying at the frontier of homogeneous and heterogeneous catalysts, offer multiple benefits of atom economy, remarkable stability, enhanced activity, better selectivity, recoverability, reusability, and energy efficiency, thereby allowing optimum feedstock utilization and minimal chemical waste. However, with time, it was diagnosed that some of these very active nanocatalysts suffer with the limitation of stability causing them to agglomerate during catalysis, which was later resolved to a great extent by modifying their surface composition via functionalization. The functionalization of these nanocatalysts with various biocompatible and active species serving as weak ligands not only enhances their stability and selectivity but also facilitates their easy separation along with preventing their undue coagulation during catalysis. Besides these, the functionalization of nanomaterials also has considerable effect reflected in their structure, morphology, optical, electrical, magnetic, and other properties owing to the novel theory of quantum effects, enabling a control of their catalytic activity.

This Chapter will cover nanocatalysis, factors affecting catalytic performance, different functionalization strategies and application of these functionalized nanocatalysts in various fields.

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Chaudhery Mustansar Hussain, Sudheesh K. Shukla and Bindu Mangla (eds.) Functionalized Nanomaterials for Catalytic Application, (355–416) © 2021 Scrivener Publishing LLC