ज्ञान-विज्ञान विमुक्तये

UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI – 110 002.

EXECUTIVE SUMMARY ON UGC MAJOR RESEARCH PROJECT (2013-2017)

(Ref. No. F.42-804/2013 (SR) dated 14. 03. 2013)

1. NAME AND ADDRESS OF THE PRINCIPAL INVESTIGATOR
   Dr. RABINDRA NATH BHOWMIK
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2. NAME AND ADDRESS OF THE INSTITUTION
   Pondicherry University,
   R. Venkataraman Nagar, Kalapet,
   Pondicherry- 605 014

3. UGC APPROVAL NO. AND DATE
   No. F.42-804/2013 (SR) dated 14. 03. 2013 and 25. 05. 2016 (extension)

4. DATE OF IMPLEMENTATION
   01. 04. 2013

5. TENURE OF THE PROJECT
   01.04.2013 to 31. 03. 2017

6. TOTAL GRANT ALLOCATED
   Rs. 17, 21, 200/- (Rupees Seventeen Lakhs Twenty One Thousand Two Hundred only)

7. TOTAL GRANT RECEIVED
   Rs. 16, 26, 840/- (Rupees Sixteen Lakhs Twenty Six Thousand Eight Hundred and Forty Only)

8. FINAL EXPENDITURE
   Rs. 15, 76, 068/- (Rupees Fifteen Lakhs Seventy Six Thousand Sixty Eight only)

9. TITLE OF THE PROJECT
   Study of the correlation between structural and magnetic heterogeneity, and semiconductivity in co rich region of $Fe_{3-x}Co_xO_4$ ferrites

10. OBJECTIVES OF THE PROJECT .....

Our main interest is to conduct detailed study of magnetism, electrical conductivity, I-V curves, electroresistance (change of resistance with electric field), magnetoresistance (change of resistance with magnetic field), & UV-visible absorption primarily at room temperature and can be extended to lower and higher temperatures depending on the interesting properties of the materials and to meet the specific objectives of the project. The objectives can be specified in the following manners.

(1) Development of Experimental Facilities in the Institute:

Measurement facilities for electrical conductivity study using Keithley meters & accessories.

(2) Proposed Materials to study

(i) $Li_{0.5}Mn_{0.5}Fe_2O_4$ spinel ferrite

(ii) $Fe_{3-x}Co_xO_4$ spinel ferrites (**x= 1.25-2.75)**

(iii) $Ni_{1.5}Fe_{1.5}O_4$ spinel ferrite

(3) Understanding of physical properties

(i) Structural (composition) analysis of the heterogeneous system

(ii) Response of homogeneous and heterogeneous magnetic systems under temperature and magnetic field variation.

(iii) Electrical response of the material under variation of dc electric field, ac electric field and temperature.

(iv) Establishment a correlation between crystal structure, magnetic, electronic, and electro-magnetic properties of the proposed magnetic materials.

(4) Development of Application oriented magnetic materials

From application point of view, our objective will be to identify suitable composition of $Fe_{3-x}Co_xO_4$ series (Co rich side) and some specific magnetic, dielectric and electronic parameters, which may be useful for application in micro-electronics devices, e.g., electric switching, magnetic sensor, power electronics, micro-wave devices, and non-linear spintronic devices.

11. WHETHER OBJECTIVES WERE ACHIEVED .....

Yes, the objectives were achieved more than 90% as projected in the work.

12. ACHIEVEMENTS FROM THE PROJECT .....

(i) Development of an advanced electrical measurement facilities in PI's laboratory using High resistance meter and accessories.

(ii) Study of magnetic properties, electrical conductivity, I-V curves, electroresistance, magnetoresistance, and electronic bipolar switching in spinel ferrites.

(iii)The work helped to gather more information about Co rich ferrite $Fe_{3-x}Co_xO_4$ and other spinel ferrites to understand the correlation between crystal structure (phase stability, grain morphology) and magnetic, electronic, and electro-magnetic properties.

(iv) This work also observed the role pH variation during chemical synthesis of material and post heat treatment on controlling the structure, grain morphology, magnetic, dielectric, electronic and optical properties in spinel ferrites.

(v) This work also reported few novel magnetic properties (exchange bias effect and distribution of magnetic exchange interaction around the blocking temperature of ferrimagnetic particles), dielectric properties (low dielectric loss, grain and grain boundary contributions in electrical conductivity and dielectric relaxation, metal like state in between low temperature and high

temperature semiconductor states), and exciting electronic properties (large electroresistane, magnetoresistance, bipolar electronic switching, and non-volatile memory effects, I-V loop). These properties are highly useful for application micro-electronic devices.

13. SUMMARY OF THE FINDINGS .....

- Single phased polycrystalline cubic spinel $Li_{0.5}Mn_{0.5}Fe_2O_4$ ferrites have been prepared by solid state sintering technique. The samples exhibited micron sized grains with strained and ring shaped surface microstructure, which became prominent at higher sintering temperature. Above 800K ac conductivity curves showed transition from semiconductor to metallic state. The dc conductivity of the samples followed variable range hopping model. A transition of charge carriers from localized state in super exchange paths (Fe^{3+}-O-Fe^{3+}, Mn^{3+}-O-Mn^{2+}) to delocalized state has been realized due to increasing semi-elastic/ visco-elastic nature of metal-oxygen bonds at higher temperatures that increased overlapping of electronic orbitals from adjacent ions.
- It is observed that microstructural parameters in $Ni_{1.5}Fe_{1.5}O_4$ ferrite strongly depend on pH value during co-precipitation and subsequent annealing. Soft ferromagnetic properties of samples can be tuned by varying pH value, which is interesting for room temperature applications of ferrite. Conduction occurs through small polaron hopping and overlapping large poloron tunneling at low temperature and high temperature respectively. The mechanism of electrical conduction in the material is same as that of dielectric polarization and is followed in the annealed samples.
- Electrical properties of the samples are influenced by the microstructure and cation redistribution in $Co_{1.25}Fe_{1.75}O_4$. The dielectric properties are controlled by charge hopping mechanism between Co^{3+}- Co^{2+} and Fe^{2+}- Fe^{3+} ions in B-sites of cubic spinel structure. High electrical conductivity and dielectric constant observed for low temperature annealed samples, due its microstructure with large imperfections and less crystallinity. Less dielectric loss of the samples at high frequency makes it suitable for high frequency communication applications. Current-Voltage loops of sample shows irreversibility and this class of materials can be used for memory applications.
- The conduction mechanism in $Co_{1.75}Fe_{1.25}O_4$ composition annealed at different temperature is governed by small polaron hopping and overlapping polaron tunneling. Asymmetric nature of M'(ν) curve predicts non de-Bye kind of relaxation mechanism. Hopping of thermally activated ions cause high dielectric loss at higher temperatures and conductive effects are suppressed at higher frequency. Variation in the distribution of Co and Fe ions in spinel structure leads to a distribution of magnetic exchange interactions and anisotropy. Semiconducting nature of sample confirmed from IV characteristics.
- The magnetic properties of $Co_{2.25}Fe_{0.75}O_4$ ferrite strongly depends on structural change associated with the variation of annealing temperature, time and atmosphere. Vacuum annealed $Co_{2.25}Fe_{0.75}O_4$ showed enhanced ferromagnetic properties. The present ferrite material may be used as a potential candidate for natural nano-composite (mixture of two spinel phases in lattice structure).
- Ferrimagnetic properties of air annealed $Co_{2.25}Fe_{0.75}O_4$ the samples are affected by configuration and stabilization/ destabilization of structural phase. The M_S and coercivity in bi-phased/tri-phased samples are correlated to Fe rich phase and Co rich phase of spinel structure, respectively.

- $Co_{2.75}Fe_{0.25}O_4$ was prepared and cubic spinel phase is confirmed. It is a soft magnetic material and its squareness is less than 1. $Co_{2.75}Fe_{0.25}O_4$ samples annealed at different temperature are highly anisotropic. Temperature dependant IV characteristics of Co rich ferrites confirm their semiconducting properties.

14. CONTRIBUTION TO THE SOCIETY .....

- This project work provided the opportunity to the PI to explore his expertise in the field of science and technology.
- This project work provided the opportunity to carry out some research activities, which is of current interest in international level. Based on the research output of this project work, some important publications came out which in many ways comparable to the output of many good national and international laboratories. This definitely strengthens Indian contribution to international level.
- This project work also provided the opportunity to many students and project fellows to have their experience in materials synthesis based on chemical route and mechanical alloying, first hand training on material characterization, measurement of physical parameters and properties of scientific and technological interests, and interpretation of the results.
- Experience and output of this project work will be utilized in many future projects for material development in industrial and R&D applications.
- The materials studied in this project work are potential candidates for high frequency communication and spintronic applications.
- The developed research facilities out of this project was utilized by many faculty members in the Pondicherry University and also users from outside (other Institutions).

15. WHETHER ANY PH.D. ENROLLED/PRODUCED OUT OF THE PROJECT.....

Yes (**01**), a portion of the work (study of $Ni_{1.5}Fe_{1.5}O_4$ ferrite) under this UGC project was carried out by a PhD student (Mr. K.S. Aneesh Kumar) who is awarded PhD degree on July 19, 2017 with thesis entitled "*Role of pH value during material synthesis and thermal activated microstructure on magnetic, dielectric and electrical conductivity properties in* $Ni_{1.5}Fe_{1.5}O_4$ *ferrite*".

16. NO. OF PUBLICATIONS OUT OF THE PROJECT .....

(A) International journals

1. Modified dielectric and ferroelectric properties in the composite of ferrimagnetic $Co_{1.75}Fe_{1.25}O_4$ ferrite and ferroelectric $BaTiO_3$perovskite in comparison to $Co_{1.75}Fe_{1.25}O_4$ ferrite, R.N. Bhowmik, and M.C. Aswathi, Composites Part B 160 (2019) 457–470 **(I.F. 4.92)**

2. Low temperature ferromagnetic properties, magnetic field induced spin order and random spin freezing effect in Ni1.5Fe1.5O4ferrite; prepared at different pH values and annealing temperatures, R.N. Bhowmik, K.S. Aneeshkumar, Journal of Magnetism and Magnetic Materials 460 (2018) 177–187 **(I.F.: 3.05)**

3. Role of initial heat treatment of the ferrite component on magnetic properties in the composite of ferrimagnetic Co1.75Fe1.25O4 ferrite and non-magnetic BaTiO3 oxide, R.N. Bhowmik, S. Kazhugasalamoorthy, and A.K. Sinha, Journal of Magnetism and Magnetic Materials 444

(2017) 451–466. **(I.F.: 3.05)**

4. Effect of annealing temperatures on the electrical conductivity and dielectric properties of Ni1.5Fe1.5O4 spinel ferrite prepared by chemical reaction at different pH values, K S Aneesh Kumar and R N Bhowmik, Mater. Res. Express 4 (2017) 126105. **(I.F.: 1.16)**

5. Electrical conductivity and magnetic field dependent current-voltage characteristics of nanocrystalline nickel ferrite P. Ghosh, R.N. Bhowmik, M.R. Dasa, P. Mitraa, Physica E 88 (2017) 218–227. **(I.F.: 2.40)**

6. Improvement of room temperature electric polarization and ferrimagnetic properties of $Co_{1.25}Fe_{1.75}O_4$ ferrite by heat treatment R.N. Bhowmik, A.K.Sinha, Journal of Magnetism and Magnetic Materials 421(2017)120–131. **(I.F.: 3.05)**

7. Role of pH value during chemical reaction, and site occupancy of Ni^{2+} and Fe^{3+} ions in spinel structure for tuning room temperature magnetic properties in $Ni_{1.5}Fe_{1.5}O_4$ ferrite K.S. Aneesh Kumar, R.N.Bhowmik, Sami H.Mahmood, Journal of Magnetism and Magnetic Materials 406(2016)60–71. **(I.F.: 3.05)**

8. Role of pH value during material synthesis and grain-grain boundary contribution on the observed semiconductor to metal like conductivity transition in $Ni_{1.5}Fe_{1.5}O_4$ spinel ferrite, R.N. Bhowmik, K.S. Aneesh Kumar, Materials Chemistry and Physics 177 (2016) 417-428. **(I.F.: 2.21)**

9. Air annealing effects on lattice structure, charge state distribution of cations, and room temperature ferrimagnetism in the ferrite composition $Co_{2.25}Fe_{0.75}O_4$ Manas Ranjan Panda, RN Bhowmik, Harishchandra Singh, MN Singh and AK Sinha, Mater. Res. Express 2 (2015) 036101. **(I.F.: 1.16)**

10. Structural phase change in $Co_{2.25}Fe_{0.75}O_4$ spinel oxide by vacuum annealing and role of coexisting CoO phase on magnetic properties R.N. Bhowmik, Manas Ranjan Panda, S.M. Yusuf, M.D. Mukadam, A.K. Sinha, Journal of Alloys and Compounds 646 (2015) 161-169 **(I.F.: 3.78)**

11. Micro-structural characterization and magnetic study of $Ni_{1.5}Fe_{1.5}O_4$ ferrite synthesized through coprecipitation route at different pH values, K.S. Aneesh Kumar, R.N. Bhowmik, Materials Chemistry and Physics 146 (2014) 159-169 **(I.F.: 2.21)**

12. Study of microstructure and semiconductor to metallic Conductivity transition in solid state sintered $Li_{0.5}Mn_{0.5}Fe_2O_4$ spinel ferrite, R. N. Bhowmik and G.Vijayasri, Journal of applied physics 114, 223701 (2013). **(I.F.: 2.18)**

Few more papers are under preparation stage and they will be published in journals.

Conference proceedings (Refereed journals)

1. Semiconductor to Metallic Type Transition in $Ni_{1.5}Fe_{1.5}O_4$ Ferrite, Aneeshkumar K.S and R. N. Bhowmik AIP Conf. Proc. 1731, 110015-1–110015-3; doi: 10.1063/1.4948036.

2. Semiconductor to metallic type transition in $Ni_{1.5}$ $Fe_{1.5}O_4$ ferrite, Aneesh kumar K. S. and R. N. Bhowmik AIP Conference Proceedings **1731**, 110015 (2016).
3. Structure and magnetic properties of the composite of $Co_{1.75}Fe_{1.25}O_4$ and $BaTiO_3$, S. Kazhugasalamoorthy and R. N. Bhowmik, AIP Conference Proceedings **1665**, 130060 (2015).
4. Existence of Fe^{4+} ions in $Co_{2.25}Fe_{0.75}O_4$ spinel ferrite confirmed from SXRD and XANES spectroscopy, Manas Ranjan Panda, R. N. Bhowmik, and A. K. Sinha
AIP Conference Proceedings 1665, 050161 (2015).

22/07/2022

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