

**FINAL REPORT**  
OF THE  
**UGC MAJOR RESEARCH PROJECT**  
**F.No. 41-371/2012(SR), dt. 16.07.2012**

**DEVELOPMENT AND CHARACTERISATION OF  
NANO MIXED OXIDES CONTAINING COPPER  
COBALT AND IRON AND STUDY OF THEIR  
CATALYTIC ACTIVITY**

Submitted to  
**THE UNIVERSITY GRANTS COMMISSION**  
Bahadur Shah Zafar Marg,  
New Delhi - 110 002

By  
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**UNIVERSITY GRANTS COMMISSION  
BAHADUR SHAH ZAFAR MARG  
NEW DELHI 110 002**

**FINAL REPORT OF THE WORK DONE ON MAJOR RESEARCH PROJECT**

1.	Project Report No.	:	<b>FINAL</b>
2.	UGC Reference No.	:	F.No. 41-371/2012(SR), dt. 16.07.2012
3.	Period of Report	:	From 01.07.2012 to 31.12.2015
4.	Title of Research Project	:	<b>Development and Characterisation of Nano Mixed Oxides Containing Copper Cobalt and Iron and Study of Their Catalytic Activity</b>
5.	(a) Name of the Principal Investigator	:	<b>Dr. S. Paul Douglas</b>
	(a) Name of the Co-Investigator		<b>Prof. B. Venkateswara Rao</b>
	(b) Department and University where work has progressed	:	Department of Engineering Chemistry, AU College of Engineering (A) Andhra University <b>Visakhapatnam 530 003 (AP)</b> Email: pauldouglas12@gmail.com Phone: 09347098430 (M); 0891-2796290 (Res)
6.	Effective date of starting of the project	:	01.07.2012
7.	Grant approved and expenditure incurred during the period of the report:		
	(a) Total amount approved	:	<b>Rs. 12,91,639/-</b>
	(b) Total expenditure	:	<b>Rs. 10,48,176/-</b>

**UNIVERSITY GRANTS COMMISSION  
BAHADUR SHAH ZAFAR MARG  
NEW DELHI 110 002**

**SUBMISSION OF INFORMATION AT THE TIME OF SENDING THE FINAL  
REPORT OF THE WORK DONE ON THE PROJECT**

1.	Name and address of the Principal Investigator	:	<b>Dr. S. Paul Douglas</b>
2.	Name and address of the Institution	:	Department of Engineering Chemistry AU College of Engineering (A) Andhra University Visakhapatnam 530 003 Email: pauldouglas12@gmail.com
3.	UGC Approval No. and Date	:	F.No. 41-371/2012(SR), dt. 16.07.2012
4.	Date of implementation	:	01.07.2015
5.	Tenure of the Project	:	Three years
6.	Total grant allocated	:	<b>Rs. 14,77,800/-</b>
7.	Total grant received	:	<b>Rs. 12,91,639/-</b>
8.	Final expenditure	:	<b>Rs. 10,48,176/-</b>
9.	Title of the Project	:	<b>Development and Characterisation of Nano Mixed Oxides Containing Copper Cobalt and Iron and Study of Their Catalytic Activity</b>
10.	Objectives of the Project:	:	<ol style="list-style-type: none"> <li>1. To prepare various copper and cobalt substituted spinel ferrites by soft-chemical routes.</li> <li>2. To characterise the fabricated nano ferrites with various physicochemical and spectroscopic methods</li> <li>3. To investigate the extent of catalytic applications</li> </ol>
11.	Whether objectives were achieved	:	All the objectives were achieved
12.	Achievements from the project:	:	<ul style="list-style-type: none"> <li>• Preparation of a series of ferrosinels containing Cu and Co having a general formula <math>Cu_{1-x}Co_xFe_2O_4</math> ( where <math>x = 0, 0.25, 0.50, 0.75</math> and <math>1</math>) by co-precipitation sol-gel method.</li> <li>• Characterization of <math>Cu_{1-x}Co_xFe_2O_4</math> by physicochemical and spectroscopic methods such as FT-IR, XRD, SEM,</li> <li>• Evaluation of the catalytic activity of the systems for the one-pot synthesis of tri-substituted imidazoles and polyfunctionalized pyridines have been commenced</li> </ul>

13.	Summary of the Findings	:	
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### **Introduction:**

Nano particles are often defined as materials that have one or more dimensions in less than 100 nm and as a result, generally have novel properties different from their bulk counterparts or atomic / molecular constituents. In recent times, there has been ongoing research into nano particulate materials because of their small size and subsequently high surface to volume ratio. The field of nano science has experienced exponential growth year-on-year due to emerging synthetic routes as well as the availability of new tools for characterisation. The 2016 Nobel Prizes in Physics and Chemistry highlight the development and importance of path breaking discoveries in nano materials for the future and benefit of the mankind.

Nano catalysis helps in designing novel catalysts with excellent activity, greater selectivity and high stability. These characteristics can easily be achieved by tailoring the size, shape, morphology, composition, electronic structure, and thermal and chemical stability of the particular nano material. Nano catalysts enjoy several advantages over conventional catalyst systems; however, isolation and recovery of these tiny nano catalysts from the reaction mixture is not easy. To overcome this issue, the use of magnetic nanoparticles has emerged as a viable solution; their insoluble and paramagnetic nature enables easy and efficient separation of the catalysts from the reaction mixture with an external magnet.

The high catalytic activity of transition metal oxides appears to be one of the most significant facts of heterogeneous catalysis. Ferrites, which are a class of magnetic oxide components that contain iron oxide as a major component has got numerous applications in electronics and electronic applications and communication devices. The magnetic properties and the strong acidic and basic sites of these ferrites paved way for developing new applications in catalysis.

## **Nano Particles**

Nano particles are often defined as materials that have one or more dimensions in less than 100 nm and as a result, generally have novel properties different from their bulk counterparts or atomic / molecular constituents [1]. In recent times, there has been ongoing research into nano particulate materials because of their small size and subsequently high surface to volume ratio. The field of nano science has experienced exponential growth year-on-year due to emerging synthetic routes as well as the availability of new tools for characterisation [2]. The 2016 Nobel Prizes in Physics and Chemistry highlight the development and importance of path breaking discoveries in nano materials for the future and benefit of the mankind.

One of the most stimulating features of nanotechnology is its potential use in almost any field. The discovery of nano particles (NPs) with varied size, shape and composition has stretched the limits of technology in ways that scientists would never have dreamt of a century ago. Nature makes and chemistry reshapes, huge varieties of nano particles have emerged in our daily life, in every field from drugs and electronics to paints and beauty care and nano materials have found applications in different fields including electronic devices, storage devices, computer modelling, catalysis, solar system, biological labelling, environmental remediation, drug delivery. This can be attributed to the fact that when the size of a crystal is decreased to the nanometre range, the electronic structure is changed from continuous bands to discrete or quantized electronic levels. Consequently, the continuous optical transitions in the molecule become quantized and therefore their properties become size controlled [3]. This in turn leads to changes in chemical features such as electronic, structural, spectroscopic, magnetic and thermodynamic [2].

## **Ferrites**

Ferrites or ferromagnetic oxides are ceramic magnetic materials, dark, brown or grey in appearance, hard and brittle in character and have high resistivities as compared to metals and alloys. The first synthetic ferrites [4] were

prepared in 1909 when there was a demand for magnetic materials. Snoeck [5] laid the foundations of physics and technology of ferrites in 1946 and undertook a systematic study [6] as a result of which a new industry came into existence. The basic theory of ferrites magnetism developed by Neel [7] was the starting point for the rapid expansion of research activity in the field of ferrites. The main motivation of the extensive study of these ferrites was the requisite combination of suitable properties to develop magnetic materials, which could show minimum current losses with superior magnetic and micro structural properties. Ferrites, which possess a wide range of these electrical magnetic and micro structural properties, are the most suitable materials for such a requirement and hence find a large number of applications in electronics, telecommunications and other industries. For four decades ferrite components have been used in an ever widening range of applications and in steadily increasing quantities. The crystallography, electrical and magnetic properties of ferrites depend upon the chemical composition as well as on the various heat treatments during the course of preparation. These properties are also influenced obviously by their method of preparation.

### **Spinel Ferrites**

The spinel ferrites are a large group of oxides which possess the structure of the natural spinel  $MgAl_2O_4$ . Spinel oxides containing iron (III) are called ferros spinels. The interesting electrical, magnetic and catalytic properties of these compounds are governed critically by their chemical composition. Simple ferros spinels ( $AFe_2O_4$ ), as well as mixed ferrite spinels of the general formula  $A^{II}_{1-x}B^{III}_xFe_2O_4$  are known. The interesting structural, electrical, magnetic and catalytic properties of these compounds are governed by their chemical composition. Special care is taken in the preparation stages of these compounds to get ferros spinels with specific properties [8].

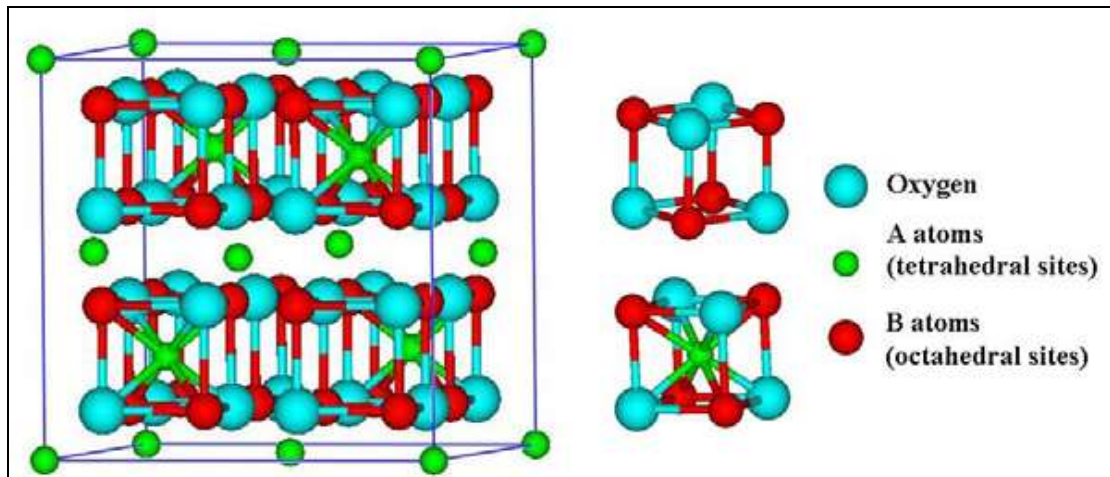


Figure 1 Unit cell of cubic spinel crystal structure  $AB_2O_4$

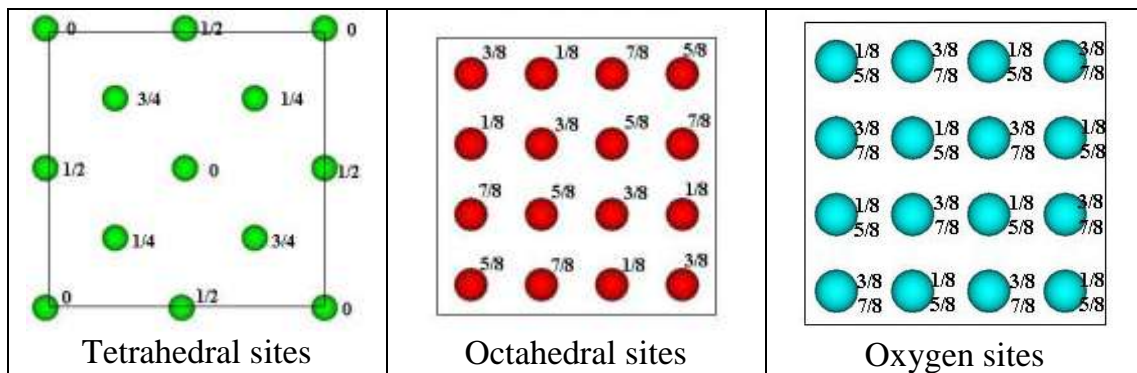


Figure 2 Projection of the spinel ionic positions on to a cube face for a perfect system where the oxygen parameter  $u = 3/8$ . Numbers give the ion positions perpendicular to a cube face as a fraction of the cube edge.

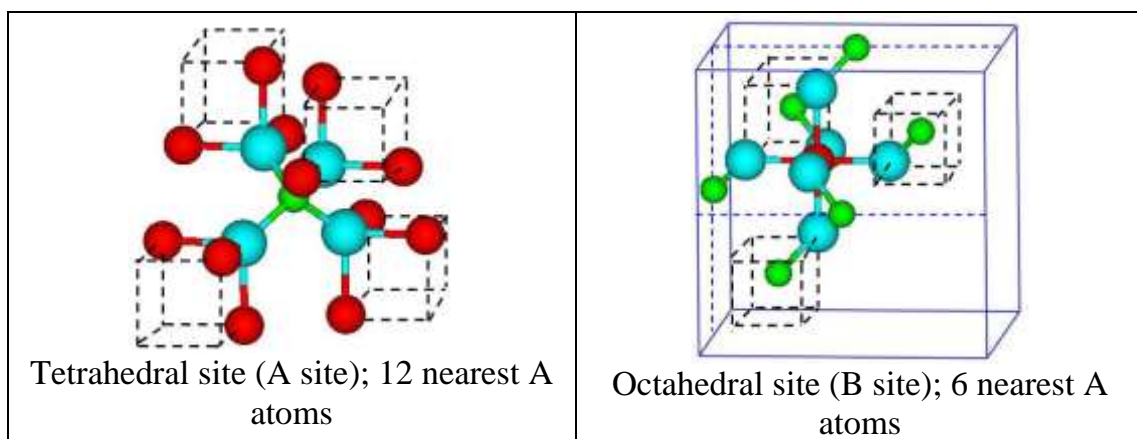


Figure 3 Schematic diagram illustrating the local atomic arrangements for (a) tetrahedral site and (b) octahedral site in spinel structure.

**Figures 1, 2 and 3** [9-10] show the unit cell and its projection on the base plane of the cubic spinel structure, in which two types of sub cells alternate in a three-dimensional array, so that each fully repeating unit cell requires eight sub cells. Two kinds of sub cells are indicated, one of which is a tetrahedral site in the body centre (green) and the other one of which is an octahedral site (red). Each A atom in a tetrahedral site has 12 nearest B atoms and each B atom in an octahedral site has 6 nearest A atoms. In the case when both A and B atoms are magnetic elements, there is an exchange interaction between A and B atoms and the number of nearest neighbour exchange interactions should also be different for each site. This difference in number of exchange interactions, depending on the crystallographic position of each magnetic element, may give physically important meaning for interpreting the magnetic properties of this material because exchange interactions among magnetic elements are the fundamental reason for magnetic ordering of magnetic materials. For this reason, the magnetic properties of cubic spinel ferrites are known to be strongly related to the cation distribution between tetrahedral and octahedral sites [9].

The general chemical formula of spinel structure is given by  $(A_x B_{1-x}) [A_{1+x} B_{1-x}] O_4$  where cations inside the parenthesis “( )” are indicated to be in tetrahedral sites and those inside the bracket “[ ]” are in octahedral sites. x varies from 0 to 1 depending on the materials; When  $x = 1$  the material is called normal spinel. When  $x=0$  the material is called inverse spinel. When  $0 < x < 1$  the material is called mixed spinel [9]. Datta and Roy [11] and Hafner and Laves [12] have shown that there are many ‘intermediate’ or ‘random’ spinels which are in between the normal and inverse arrangements. These intermediate spinels are normally labelled in terms of the percent inverse character that they exhibit. **Table 1** illustrates some of the examples of normal, inverse and intermediate spinels.



**Table 1: Examples of some normal and inverse spinels**

Type	Structure	Examples
Normal	$[A^{2+}B^{3+}_2]O_4$	ZnFe <sub>2</sub> O <sub>4</sub> , ZnCrFeO <sub>4</sub> , ZnCr <sub>2</sub> O <sub>4</sub> ,
Inverse	$B^{3+}[A^{2+}B^{3+}]O_4$	MgFe <sub>2</sub> O <sub>4</sub> , NiFe <sub>2</sub> O <sub>4</sub> , CoFe <sub>2</sub> O <sub>4</sub>
Random	$(A^{2+}_x B^{3+}_y)[A^{2+}_{2-y} B^{3+}_{2-y}]O_4$	Ni <sub>0.5</sub> Zn <sub>0.5</sub> Fe <sub>2</sub> O <sub>4</sub>

On the basis of crystal structure, ferrites are classified into four main classes - cubic or spinel ferrites, hexa ferrites, ortho ferrites and garnets. On the basis of technical application, ferrites are categorized as soft ferrites and hard ferrites. Soft ferrites are dark grey or black ceramic materials. They are very hard, brittle and chemically inert. Most magnetically soft ferrites have spinel structure. Soft ferrites are by far the most widely used ferrites, so much that the term is almost synonymous with the word ferrite [13].

### Nano Magnetic Ferrites as Catalysts

The term “catalysis” was introduced by Berzelius in 1836. Ostwald, one of the first Noble prize winners in chemistry (1905) suggested a definition (in 1895) which is valid even today “a catalyst accelerates a chemical reaction without affecting the position of the equilibrium”. It was formerly assumed that the catalyst remained unchanged. For the present time, certainly, we know that the catalyst is involved to chemical bonding with the reactants during the catalytic process, the reactants are bound to one form of the catalyst and the products are released from another, regenerating the initial state. Heterogeneous catalysis is an integral part of the modern technology, since about 80% of all industrial chemicals are manufactured by catalytic reactions.

Ternary oxides crystallizing with spinel structure exhibit interesting catalytic properties. The spinel lattice imparts extra stability to the catalyst under various reaction conditions, so that these systems sustained activity for longer periods [14]. In spinel systems correlation between catalytic activities and the electric and the magnetic properties are often found, this is a direct consequence of the dependence of both properties on the nature of the ions, their charges and their

distributions among octahedral and tetrahedral sites. Courty, *et al.* in their work revealed that octahedral sites are exposed almost exclusively at the surface of spinel [15]. The tetrahedral ions are either inactive or contributing only a little to the catalytic properties. The lower activity of the tetrahedral ions comes from the fact that the metal oxygen bonds will be stronger due to lower coordination number and hence such cations are less accessible to the reactants. Among the spinel compounds, ferrites have been used as effective catalysts for a number of industrially important reactions such as oxidative dehydrogenation of hydrocarbons [16-18], hydrodesulphurization of petroleum crude [19-20], oxidation of CO [21], etc. The catalytic effectiveness of ferrites for many such reactions arises because of the ease with which iron can exchange its oxidation state between 2 and 3. Even if reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  occurs, spinel structure remains unaltered and upon reoxidation the original state can be regained [22].

Further, as size decreases, the surface area to volume ratio increases. Therefore, nanocatalysts are small in size and have an enormous surface area to volume ratio. The available surface area of the active component of a nanocatalyst is large. Therefore, it increases contact between the reactant molecules and the catalyst to a great extent. This enhanced interaction facilitates the heterogeneous catalytic system and helps to achieve a better reaction rate that is closer to its homogeneous counterpart. Easy control of nanocatalysts over size, shape and morphology makes it possible to rationally design the materials that are specifically needed for a particular catalytic application. Thus, tuning the properties of a material is easily possible when working at the nanoscale, which would be difficult with their macroscopic counterparts.

Catalyst recovery and reuse are the two most important features for many catalytic processes, and most heterogeneous systems require a filtration or centrifugation step and/or a tedious workup of the final reaction mixture to recover the catalyst. However, magnetically supported catalysts can be recovered with an external magnet as shown in **Figure 4** due to the paramagnetic character of the support, resulting in remarkable catalyst recovery without the need for a filtration

step. In addition to all the above, magnetic nanoparticles can serve as a highly useful catalyst support enabling immobilization and magnetic recovery of the catalyst [9].



**Figure 4: Separation of magnetically separable catalyst from the reaction mixture using an external magnet**

The catalysts can be subsequently reused in another cycle. Magnetically separable catalysts also offer important activities in a wide range of reactions due to their potential for designed surface functionalities along with catalyst preparation [10].

### **Nano Copper-Cobalt Ferrites as Catalysts**

Cobalt ferrite has been extensively investigated because of its interesting magnetic behaviour, chemical stability and mechanical hardness [23-24]. Cobalt ferrite ( $\text{CoFe}_2\text{O}_4$ ), crystallizes in a partially inverse spinel structure [25]. Nano size ferrites have been prepared by various techniques such as sol-gel combustion, modified oxidation process, forced hydrolysis, hydrothermal process, ball milling and the micro-emulsion method [26-31]. On the other hand cobalt ferrite is a promising candidate material for biomedical drug delivery [32], magnetic

resonance imaging [33], biocompatible magnetic nano particles for cancer treatment [34] and magneto-optical devices [35]. Many of these (soft and hard magnetic) properties make them very promising candidates for different applications in electronic (recording technology) and in biomedicines [36-39].

The use of magnetic nano particles (MNPs) as a catalyst support in organic synthesis, the recovery of expensive catalysts after catalytic reaction and reusing them without losing their activity is an essential feature in the sustainable process development. The surface properties and catalytic activity of ferros spinels of nickel, cobalt, copper and their sulphated analogues are prepared by soft chemical methods at the room temperature coprecipitation route to yield samples with high surface areas. The intrinsic acidity among the ferrites is found to decrease in the order of cobalt > nickel > copper. Electron donor studies revealed that copper ferrite has both the highest proportion of strong sites and the lowest proportion of weak basic sites. All the ferrite samples proved to be good catalysts for the benzylation of toluene with benzoyl chloride. Copper and cobalt ferrites being much more active than nickel ferrite. Surface Lewis acid sites, provided by the octahedral cations on the spinel surface are suggested to be responsible for the catalytic activity for the benzylation reaction [40].

A series of  $\text{Cu}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$  ( $x = 0, 0.25, 0.5, 0.75$  and  $1.0$ ) ferros spinels has been used in the gas phase alkylation of phenol. The reaction conditions are optimized to give a maximum yield of 2,6-xyleneol over o-cresol. Various structural changes are observed due to exposure of the fresh catalysts to the reaction mixture. Namely, phase separation to CuO and magnetite in the  $x = 0$  and  $0.25$  samples, various extents of reduction (changing monotonically with the copper content and resulting in partial reduction and redistribution of iron in tetrahedral (A) and octahedral (B) sites) and extended formation of carbonaceous deposits studied [41].

Acid–base properties of  $\text{Cu}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$  ferros spinels using FT-IR were undertaken to investigate the acid–base properties of Cu–Co ferros spinels  $\text{Cu}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$  ( $x = 0$  to  $1$ ) employed in phenol methylation to produce 2, 6-xyleneol.

The FT-IR spectra of the ferros spinels reveal that  $\text{Fe}^{3+}$  and  $\text{Co}^{2+}$  ions are mainly responsible for the various hydroxy groups on the surface [42].

Arsenic removal from water by magnetic  $\text{Fe}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$  and  $\text{Fe}_{1-y}\text{Ni}_y\text{Fe}_2\text{O}_4$  nano particles [43] and the effects of Co and Ni replacement in  $\text{Fe}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$  and  $\text{Fe}_{1-y}\text{Ni}_y\text{Fe}_2\text{O}_4$  ( $x, y = 0, 0.05, 0.1, 0.2$  and  $0.5$ ) nano particles, pH, weight of nano particles/mL of water and time of stirring on the arsenic removal ability are presented.

New magnetically recyclable catalysts (MRCs) with general formula  $\text{AgM}_{1-x}\text{Fe}_{2+x}\text{O}_4$  ( $M = \text{Co}, \text{Ni}, \text{Mn}, \text{Zn}$ ) have been synthesized via a generalized one-pot route and these materials prove to be efficient catalysts in the catalytic epoxidation of styrene [44]. It has been demonstrated that the ferrite supports affect the structure of Ag and the efficiency in oxygen supply and thus the catalytic performance. Asymmetric hydrosilylation of ketones catalyzed by magnetically recoverable and reusable copper ferrite nano particles is reported. Up to 99% enantiometric excess is obtained at room temperature using polymethylhydrosiloxane as the stoichiometric reducing agent. The copper ferrite nano particles are magnetically separated and the efficiency of the catalyst remains almost unaltered up to three cycles [45].

The magnetic and catalytic properties of copper ferrite nano powders prepared by combustion process are presented [46]. In this, copper ferrite nano-particles with Fe/Cu ratios varying from 2 to 12 were successfully synthesized by combustion process using copper nitrate, iron nitrate and urea. These copper ferrite magnetic nano-particles also acts as catalyst for the oxidation of 2,3,6-trimethylphenol to synthesize 2,3,5-trimethylhydrogenquinone and 2,3,5-trimethyl-1,4-benzoquinone for the first time. The reaction shows dramatically enhanced by the addition of copper-ferrite nano-particles to the solution.

Magnetically recoverable nano copper ferrite catalyst ( $\text{CuFe}_2\text{O}_4$ ) is used as an efficient protocol for the rapid room temperature deacetylation of carbohydrate derivatives [47]. After separation of the catalyst with an external magnet, the reaction products are easily obtained in good purity and excellent yields.

Magnetically separable and reusable copper ferrite nano particles for cross-coupling of aryl halides with diphenyl has been developed by a copper ferrite nano particle catalyzed reaction of aryl iodides/aryl bromides with diphenyl diselenide in the presence of base and solvent at 120 °C. Using this protocol, a variety of diselenides is obtained in good to excellent yields. The copper ferrite nano particles are magnetically separated, recycled and reused up to three cycles [48].

Synthesis, characterization and catalytic activity of chromium substituted cobalt ferros spinels is reported and the catalytic activity of the samples is investigated towards acetylation of phenols. The presence of active centres on the surface of the material is confirmed through pyridine adsorption studies. The surface acidity of the catalyst is responsible for better catalytic performance. The material is found to serve as a promising catalyst for acylation and benzylation of phenols under solvent free condition. These catalysts are 100% selective towards O-acylation of phenols. The catalysts are seen to be reusable without any further treatment. Catalytic activities of cobalt, chromium and iron oxides are also investigated for comparison. The cobalt ferros spinel is found to have better catalytic activity as compared to the Cr substituted ferros spinels and the pure oxides. Cobalt ferrite catalyst offers high yields in a short reaction time under solvent-free conditions [49].

Magnetic and catalytic properties of cubic copper ferrite nano powders synthesized from secondary resources via a hydrothermal route using industrial wastes. Photocatalytic degradation of the methylene blue dye using copper ferrite powders produced at different conditions is investigated [50].

Magnetically retrievable catalysts for organic synthesis like Suzuki cross-coupling of deactivated aryl chloride, bromobenzene, 4-bromoanisole with phenylboronic acid, Heck reaction of aryl chlorides with styrene, Sonogashira coupling of aryl chlorides and phenyl acetylene, etc. are reported [51].

CuFe<sub>2</sub>O<sub>4</sub> nano particles as highly efficient and magnetically recoverable catalysts for the synthesis of medicinally privileged spiro pyrimidine scaffolds are presented [52]. The magnetic nature of catalyst facilitates its easy removal from

the reaction medium and can be reused five times without any significant loss of its catalytic activity. Negligible leaching of Cu and Fe in consecutive cycles makes the catalyst economical and environmentally benign.

One-pot, three-component synthesis of 1, 4-Dihydropyridines by using nano crystalline copper ferrite. Copper ferrite nano material (catalyst) are reusable heterogeneous initiator in the synthesis of 1, 4-dihydropyridines is presented [53]. The reaction of substituted aromatic aldehydes, ethyl acetoacetate and ammonium acetate is achieved in the presence of copper ferrite nano powders at room temperature in ethanol. The nano catalyst is easily recovered and its reusability is presented.

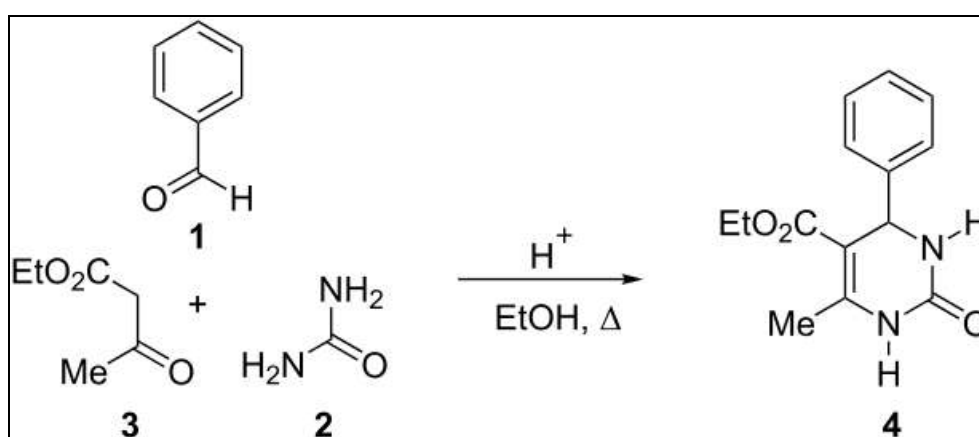
Catalytic synthesis of  $\alpha$ -Amino nitriles using nano Copper ferrite under green conditions is reported [54]. Copper ferrite nano material as reusable heterogeneous initiator in the synthesis of  $\alpha$ -aminonitriles. The nano catalyst is easily recovered and its reusability is recorded. Synthesis of  $\alpha$ -aminonitriles derivatives by one-pot reaction of different aldehydes with amines and trimethylsilyl cyanides has been developed using nano copper ferrite catalyst under room temperature and green solvent (water as solvent) conditions.

The synergistic effects of iron and copper in copper ferrite nanoparticles for the N-arylation of heterocycles with aryl halides were demonstrated. The magnetic nature of the catalyst facilitates its removal from the reaction medium for further use. Negligible leaching of Cu and Fe in consecutive cycles makes the catalyst economical and environmentally benign for C–N cross-coupling reactions. The magnetic nature of  $\text{CuFe}_2\text{O}_4$  nanoparticles is particularly advantageous for easy, quick and quantitative separation of the catalyst for reuse. This catalytic process is simple, efficient, economical and environmentally safe [55].

### **One-pot Multi-Component Reactions**

Formation of a new carbon-carbon bond is one of the most fundamental operations in organic chemistry. Multi-component reactions are the most efficient and effective methods in the sustainable and diversity-oriented synthesis of wide variety of useful compounds such as biologically active heterocyclic compounds

including pharmaceuticals. In multi-component reactions, two or more components are combined in a single reaction as shown in **Figure 5**, thereby providing an operationally effective and highly modular approach towards the synthesis of structurally diverse molecular entities. The result in Multi-component reaction is depends on reaction conditions like temperature, solvent, catalyst, concentration, the kind of starting materials and functional groups. Such considerations play a vital role in the design and discovery of novel multi-component reactions. Hence drag greater attention of chemists in generating structurally diverse organic scaffolds.



**Figure 5 Representation of one-pot multi-component reactions**

### Nano Materials as Catalysts in One-pot Multi-component Reactions

Recently, functionalized magnetic nano particles have emerged as viable alternatives to conventional materials, as robust, readily available, high-surface-area heterogeneous catalyst supports. They offer an added advantage of being magnetically separable, thereby eliminating the requirement of catalyst filtration after completion of the reaction. These nano particles are engaged in the development of greener and sustainable pathways for organic transformations [56]. Several reports shows the amazing level of the performance of nano particles as catalysts in terms of selectivity, reactivity and improved yields of products. In addition, the high surface-to-volume ratio of nano particles provides a larger number of active sites per unit area, in comparison with their heterogeneous counter sites [57, 58].



Magnetic nano particles are receiving increasing interest in recent years and are being used widely as a useful group of heterogeneous catalysts for organic synthesis due to their remarkable advantages such as the remarkable catalytic activity, easy synthesis, operational simplicity, eco-friendliness and recoverability with an external magnetic field.

Further, several copper and cobalt ferrite catalyzed reactions have been reported for the synthesis of heterocyclic compounds. They are, synthesis of spirooxindoles in water by copper ferrite nano particles [59], synthesis of  $\alpha$ -aminophosphonates by nano ferrite ( $\text{Fe}_3\text{O}_4$ ) [60], N-arylation of heterocycles by copper ferrite nano particles [61], synthesis of 5-substituted 1H-tetrazoles by copper ferrite ( $\text{CuFe}_2\text{O}_4$ ) nano particles [62], synthesis of 1, 4-disubstituted 1, 2, 3-triazoles in tap water by copper ferrite nano particles [63], oxidation of alkenes by nano cobalt ferrite [64], Synthesis of  $\alpha$ -aminonitriles by nano copper ferrite [65], synthesis of 2, 4, 5-tri substituted imidazoles by nano copper and cobalt ferrites [66], synthesis of  $\beta$ - acetamido ketones by nickel cobalt ferrite [67], synthesis of poly substituted imidazoles by nano copper ferrite [68], poly substituted pyridine derivatives by nano copper ferrite [69], 4*H*-Pyrano [3, 2-*h*] quinoline derivatives by nano cobalt ferrite [70], etc.

### **Rational of the Study and the Research Gap**

It is observed from the review of literature that there available a plethora of research being conducted all over the world to develop new catalysts and establish the procedures for the application at the lab level and in scaling up process. Very few of the available researches have been presented in this part.

Futher, keeping in view of the advantages of nano magnetic catalyst systems, many new reactions have been studied in the limited time framework of research to be completed and submitted as part of the course work. Many areas could be studied and many factors could also be considered in selecting the objectives and scope of the work, but finally keeping in view of the framework of the course, the study confined to the objectives selected.

The main aim of this research work is on the synthesis and characterisation of nano crystalline copper-cobalt ferrites and study their catalytic application in the synthesis of some new class of organic compounds by one-pot multicomponent synthesis using greener strategies. The catalysts have been prepared by soft chemical method by citrate sol-gel processes. Phase pure nano crystalline copper-cobalt ferrites with composition  $\text{Cu}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$  (where  $x=0, .25, 0.5, 0.75$  and  $1$ ). The catalysts have been characterised and used in the research as magnetically separable nano catalysts. This technique produced good yield and ensured complete homogeneity. Hence this process could be scaled.

**The objectives of the study are:**

1. To synthesise nano spinel copper-cobalt ferrites of the composition  $\text{Cu}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$  ( $x = 0, 0.25, 0.5, 0.75$  and  $1$ ) by citrate sol-gel method.
2. To characterise the synthesized nano ferrites using FT-IR, XRD, SEM, EDAX, TEM and BET surface area techniques to interpret their structure, morphology and size.
3. To apply the synthesised ferrites as heterogeneous magnetically separable catalysts and to develop process optimisation for the one-pot synthesis of  $\beta$ ,  $\gamma$ -unsaturated ketones, 3,4-dihydro-pyrimidine-2(1H)-ones/thiones,  $\beta$ -acetamido esters,  $\beta$ -acetamido ketones under ultrasonication/ reflux/ microwave irradiation.
4. To characterise the structure of the newly synthesised heterocyclic compounds using FT-IR,  $^1\text{H}$  NMR and MASS spectral analysis
5. To study the biological activity of the newly synthesised heterocyclic compounds.

## **Synthesis and Characterisation of Nano Copper-Cobalt Ferrite Catalysts:**

This chapter deals with the synthesis of copper-cobalt ferrites with composition  $\text{Cu}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$  ( $x=0, 0.25, 0.5, 0.75$  and  $1$ ) by sol-gel citrate precursor method and characterisation of the spinel nano-ferrites using FT-IR, SEM, EDAX, XRD, TEM and BET surface area methods.

Nano particles of copper-cobalt ferrites with the general formula  $\text{Cu}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$  have been synthesized by citrate sol-gel method. The FT-IR spectra show the absorption band around  $575\text{ cm}^{-1}$  which is attributed to the stretching vibrations of tetrahedral complexes. The band around  $410\text{ cm}^{-1}$  is attributed to the stretching vibrations of octahedral complexes. The XRD spectra reveal the average crystallite size to be in the range 30-40 nm and this is found to be in agreement with TEM results. The SEM micrographs show the appearance of a sponge like structure. The EDAX spectra confirm the presence of metallic compounds without impurities.

However, in many cases the nanoparticles formed get agglomerated with non uniform shape and cannot be stored for a long period. Sometimes, the particles formed are poorly crystalline and milling or high temperature annealing is required to obtain highly crystalline structure. Also, the magnetic hardening occurs only after high temperature annealing. Micro-emulsion methods are very effective for synthesizing nanoparticles with well-defined size and narrow size distribution, but these methods are not suitable to produce in large quantities. The most advantageous method for production of nano particles is the co-precipitation method where the particles were prepared by co-precipitating a mixture of cobalt(II) and iron(II) salts with hydroxide ions using potassium nitrate [39] or air as oxidizing agent. Very recently, Kulkarni and his coworkers reported a co-precipitation method for oleic acid capped  $\text{CoFe}_2\text{O}_4$  nanoparticles [46].

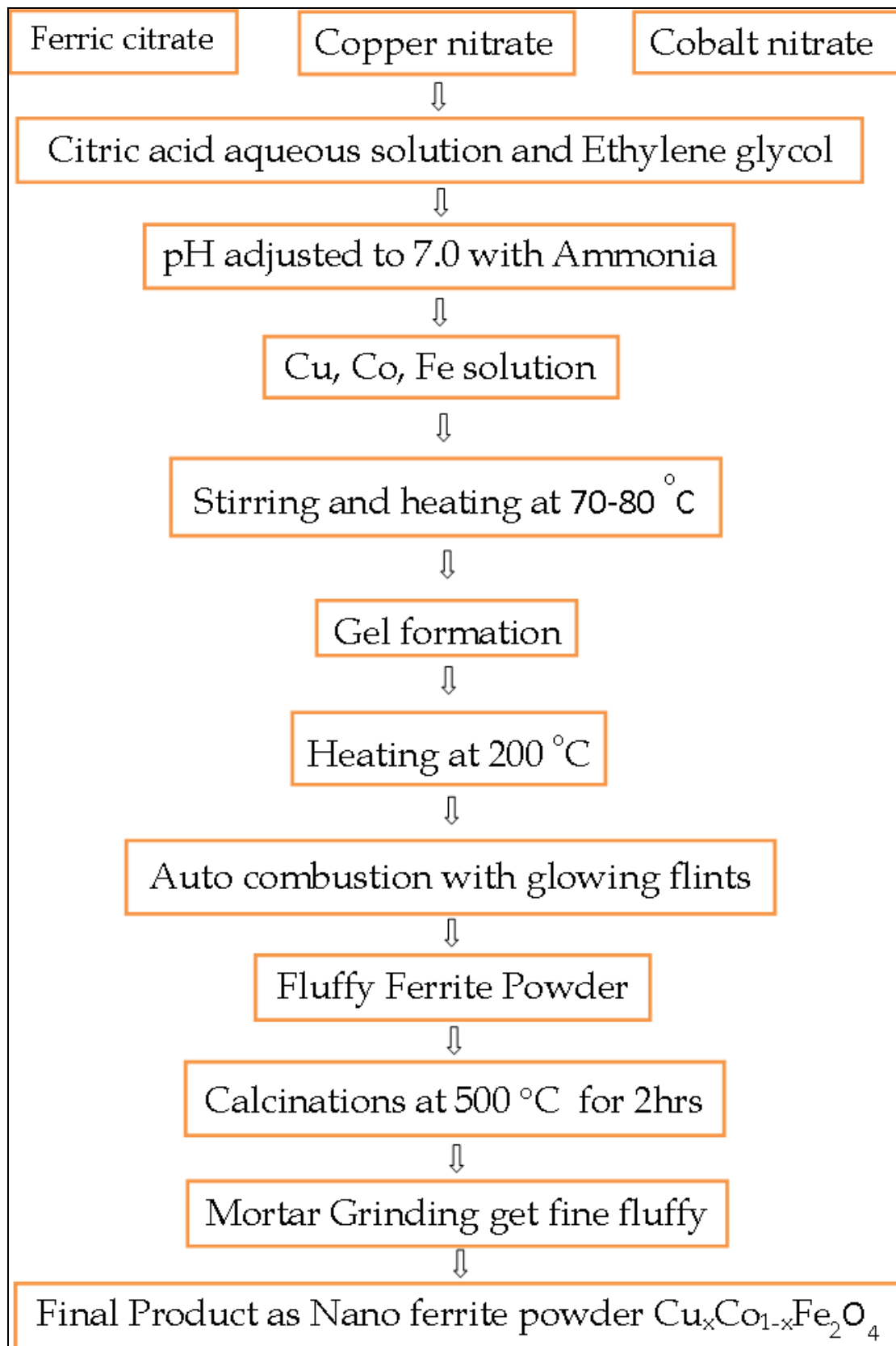
The method of synthesis of copper cobalt ferrite catalysts and structural characterisation with the help of FT-IR, XRD, SEM, EDAX, TEM techniques are presented

## Synthesis of Copper-Cobalt Ferrites

Copper-Cobalt ferrites with the general formula  $\text{Cu}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$  ( $x = 0, 0.25, 0.5, 0.75$  and  $1$ ) have been chosen for this work. Aqueous solution of stoichiometric amounts (**Table 2**), for example for  $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$  sample, copper nitrate (0.05 mole), cobalt nitrate (0.05 mole) and ferric citrate (0.1 mole) are reacted with citric acid in 1:3 molar ratio (0.3 mole), then 10 ml of ethylene glycol is added, pH of the solution is increased to 7 by addition of ammonium hydroxide to complete the reaction. The solution is evaporated very slowly over a period of ten to twelve hours to dryness. Viscosity and colour changed as the solution turned into puffy, porous dry gel (**Scheme 1 & Figure 6**). As soon as the solvent removal is completed, dried precursor undergoes a self-ignition reaction to form a very fine powder known as as-synthesized powder. The as-synthesized powder thus obtained is calcinated in a muffle furnace at  $500\text{ }^\circ\text{C}$  for 2 hours to remove the residual carbon and phase formation. These samples are characterized using FT-IR, XRD, SEM, EDAX, TEM and BET surface area analysis.

**Table 2 Weights of ingredients taken for the synthesis of Cu-Co ferrites**

General Formula $\text{Cu}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$	Amount of $\text{Cu}(\text{NO}_3)_2$ g	Amount of $\text{Co}(\text{NO}_3)_2$ g	Amount of Ferric Citrate g	Amount of Citric Acid g	Sample Composition
X = 0	12.08	0.00	29.89	31.5	$\text{CuFe}_2\text{O}_4$
X = 0.25	9.06	3.52	29.89	31.5	$\text{Cu}_{0.75}\text{Co}_{0.25}\text{Fe}_2\text{O}_4$
X = 0.5	6.04	7.28	29.89	31.5	$\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$
X = 0.75	3.06	10.54	29.89	31.5	$\text{Cu}_{0.25}\text{Co}_{0.75}\text{Fe}_2\text{O}_4$
X = 1	0.00	14.55	29.89	31.5	$\text{CoFe}_2\text{O}_4$



**Scheme 1 Scheme of synthesis of nano copper cobalt ferrites by Citrate Sol-Gel Method**



**Figure 6 Synthesis of nano copper cobalt ferrites by citrate precursor method**

The prepared samples were characterized by FT-IR, XRD, SEM, TEM, EDAX, BET Surface area analysis. Chemical compositions structural and textural properties of  $\text{CuFe}_2\text{O}_4$ ,  $\text{Cu}_{0.75}\text{Co}_{0.25}\text{Fe}_2\text{O}_4$ ,  $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$   $\text{Cu}_{0.25}\text{Co}_{0.75}\text{Fe}_2\text{O}_4$  and

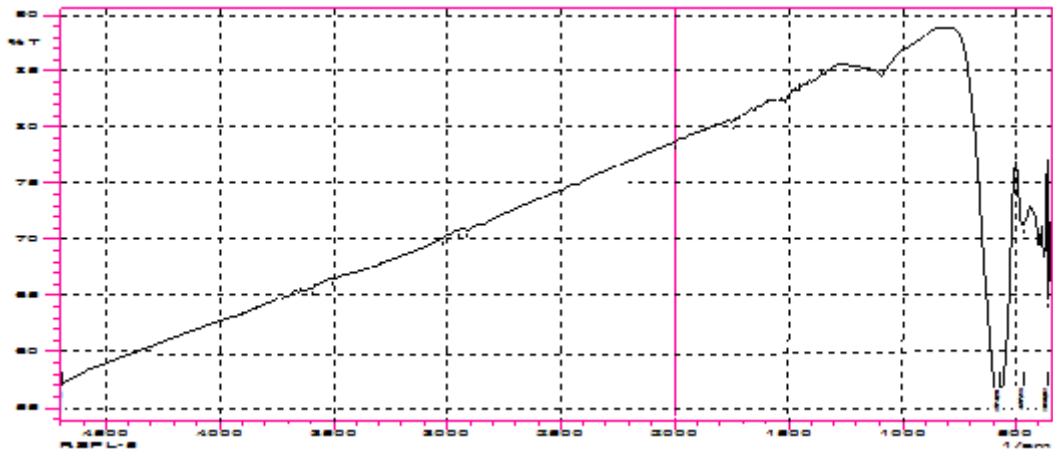
CoFe<sub>2</sub>O<sub>4</sub> spinel ferrites that are prepared in the present study are summarized below.

### **FT-IR Spectral Analysis**

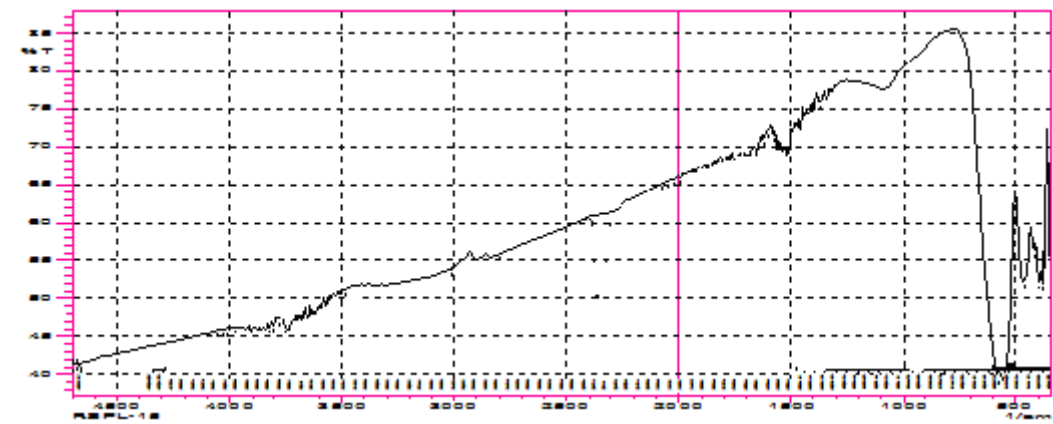
Ferrites possess the structure of spinel (MgAl<sub>2</sub>O<sub>4</sub>) that crystallizes in the cubic form [54] (White & De Angelis 1967). The magnetic properties of ferrites are decisively dependent on the precise configuration of the atoms and ions in the structure. Therefore, the non-destructive spectroscopy is especially suited for such investigations.

**Figures 7-11** shows the FT-IR spectra of the copper-cobalt ferrites of general formula Cu<sub>(1-x)</sub>Co<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> (x = 0, 0.25, 0.5, 0.75 and 1) sintered at 500 °C, recorded at wave number range 4000 cm<sup>-1</sup>-400 cm<sup>-1</sup>. According to Waldron (1955) the ferrites can be considered as continuously bonded crystals, meaning that the atoms are bonded to all the nearest neighbours by equivalent forces. In ferrites the metal ions are situated in two different sub-lattices designated tetrahedral (A-site) and octahedral (B-site) according to the geometrical configuration of the oxygen nearest neighbours [55]. Also, Waldron (1955) and Hafner & Krist (1961) have attributed the band around 600 cm<sup>-1</sup> to stretching vibrations of tetrahedral group (ν<sub>1</sub>) and that around 400 cm<sup>-1</sup> to the octahedral group (ν<sub>2</sub>). In the present study the absorption bands for copper-cobalt ferrites are found to be in expected range [56].

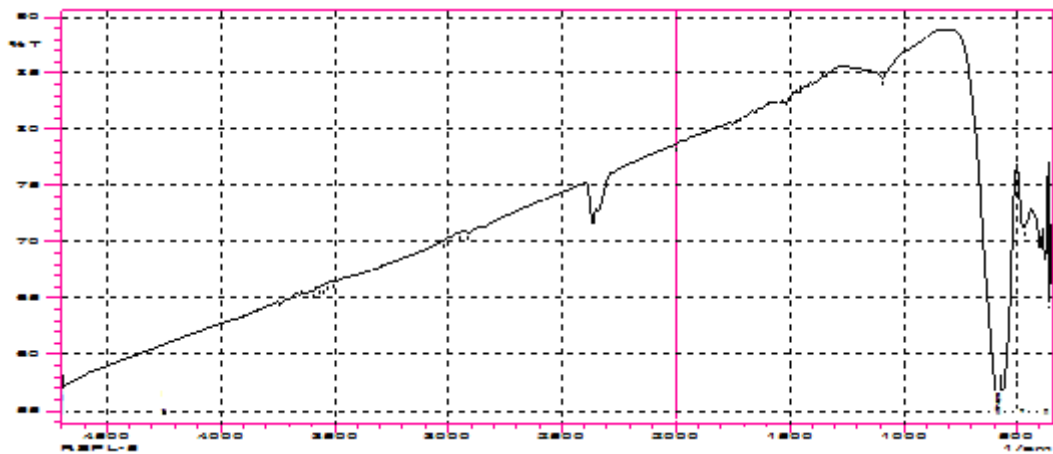
The small absorption bands around 2350 cm<sup>-1</sup> and 1020 cm<sup>-1</sup> are due to traces of adsorbed or atmospheric CO<sub>2</sub>. The main absorption band appearing around 575 cm<sup>-1</sup> is due to tetrahedral sites and is found to be shifted to higher values on doping with cobalt. The band around 410 cm<sup>-1</sup> is due to octahedral sites and is shifted to lower values upon increasing the concentration of cobalt ions. These observations may be attributed to the fact that the absorption bands for pure copper ferrite appear around 575 cm<sup>-1</sup> and 410 cm<sup>-1</sup> respectively and it is evident that the inclusion of cobalt is responsible for shifting the bands appropriately to higher values for ν<sub>1</sub> and lower values for ν<sub>2</sub>.



**Figure 7 FT-IR Spectra of CuFe<sub>2</sub>O<sub>4</sub> (A)**

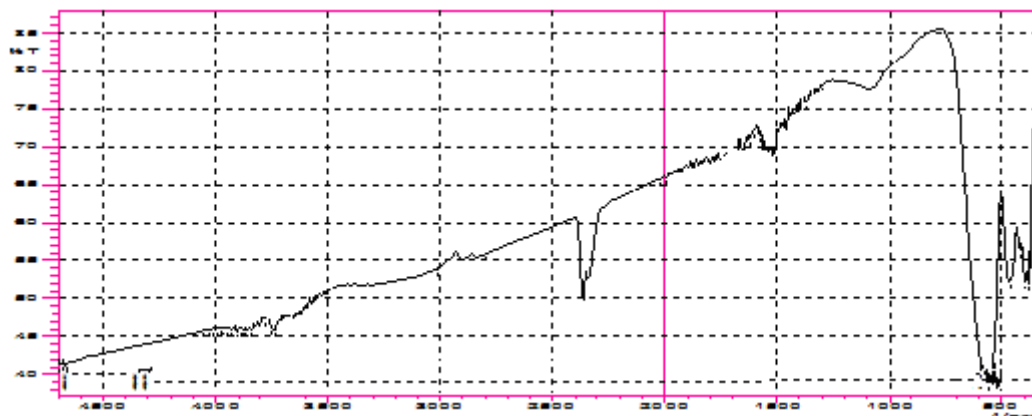


**Figure 8 FT-IR Spectra of Cu<sub>0.75</sub>Co<sub>0.25</sub>Fe<sub>2</sub>O<sub>4</sub> (B)**

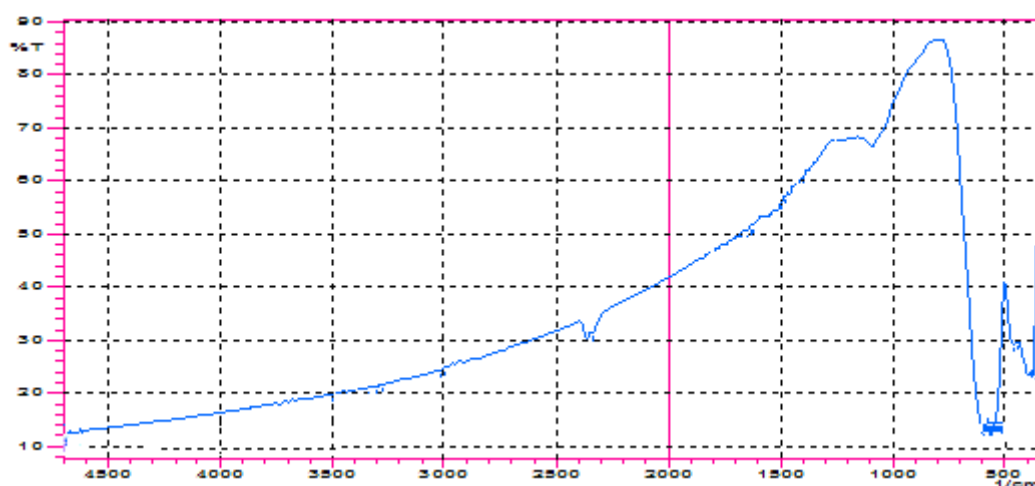


**Figure 9 FT-IR Spectra of Cu<sub>0.5</sub>Co<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> (C)**





**Figure 10 FT-IR Spectra of Cu<sub>0.25</sub>Co<sub>0.75</sub>Fe<sub>2</sub>O<sub>4</sub> (D)**



**Figure 11 FT-IR Spectra of CoFe<sub>2</sub>O<sub>4</sub> (E)**

### Structural Analysis by XRD

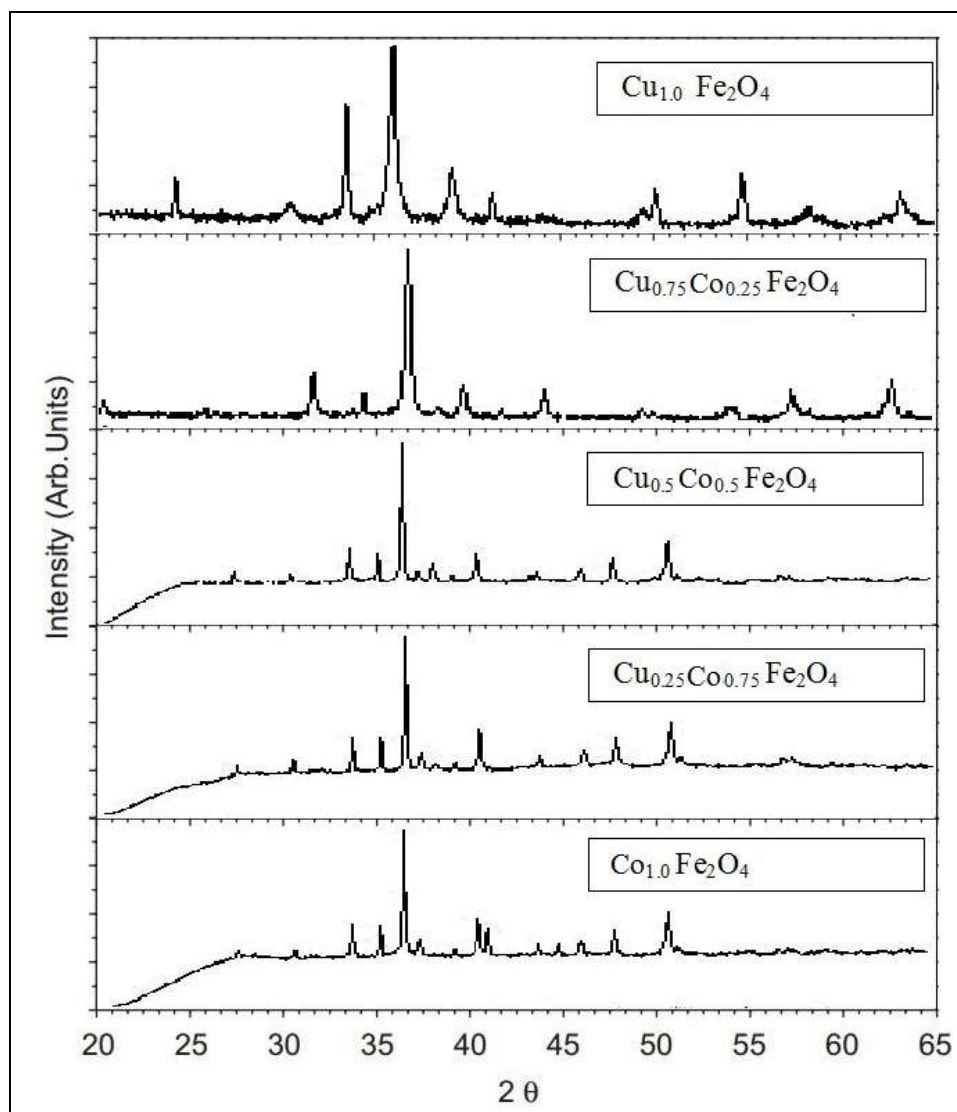
**Figure 12** shows the XRD patterns of the as-synthesised spectra of the copper-cobalt ferrites of general formula Cu<sub>(1-x)</sub>Co<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> (x = 0, 0.25, 0.5, 0.75 and 1) sintered at 500 °C. Analysis of the diffraction pattern confirms the formation of cubic spinel structure for all the samples. The experimentally observed spacing values and relative intensities are in good agreement with those reported in the powder diffraction file of JCPDS card no. (22-1086) and (34-0425) for cobalt and copper ferrites. The strongest reflection comes from the (311) plane, which denotes the spinel phase. All the compositions have a spinel structure. The peaks indexed to (111), (220), (311), (222), (400), (422), (511),

(440), (620), (533), (622), (444) and (642) planes of a cubic unit cell, correspond to cubic spinel structure.

The lattice parameters are calculated for all the compositions and are listed in **Table 2**. It is observed that the lattice parameter increase on inclusion of cobalt content as could be evidenced from **Table 2**. The increase in lattice parameter with decrease in copper content is due to the replacement of larger  $\text{Co}^{2+}$  cations with smaller  $\text{Cu}^{2+}$  cations. It is also observed that the lattice parameter decrease on further addition of cobalt. It is found that the strain is minimum for copper rich samples and increases as cobalt concentration increases. The crystallite size of each composition is then determined by the Debye-Scherrer [57-59] relation and listed in **Table 2**. It varies with the composition and is found to increase with the substitution of cobalt which indicates that the addition of cobalt has a great effect in increasing the grain growth of the spinel.

**Table 2 Lattice Parameter and Crystallite size of copper and cobalt ferrites**

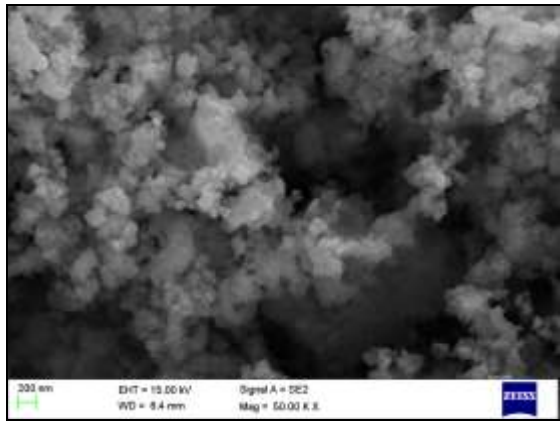
S.No	Sample	Lattice Parameter (a) Å	Crystallite Size D nm
1	$\text{CuFe}_2\text{O}_4$	8.3089	30
2	$\text{Cu}_{0.75}\text{Co}_{0.25}\text{Fe}_2\text{O}_4$	8.3092	34
3	$\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$	8.3105	36
4	$\text{Cu}_{0.25}\text{Co}_{0.75}\text{Fe}_2\text{O}_4$	8.3111	38
5	$\text{CoFe}_2\text{O}_4$	8.3116	40



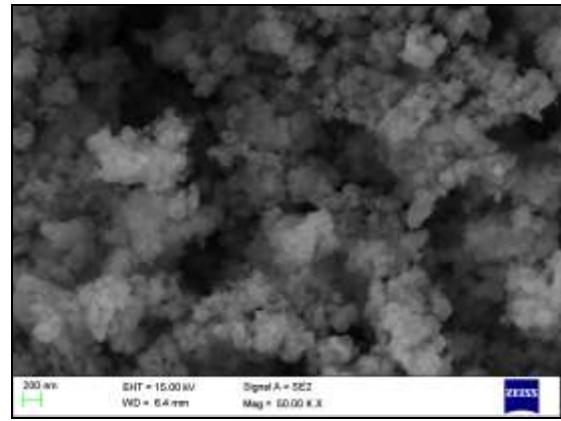
**Figure 12 XRD Spectra of (A)  $\text{CuFe}_2\text{O}_4$ , (B)  $\text{Cu}_{0.75}\text{Co}_{0.25}\text{Fe}_2\text{O}_4$ , (C)  $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$  (D)  $\text{Cu}_{0.25}\text{Co}_{0.75}\text{Fe}_2\text{O}_4$  (E)  $\text{CoFe}_2\text{O}_4$**

### **Morphological Analysis (SEM)**

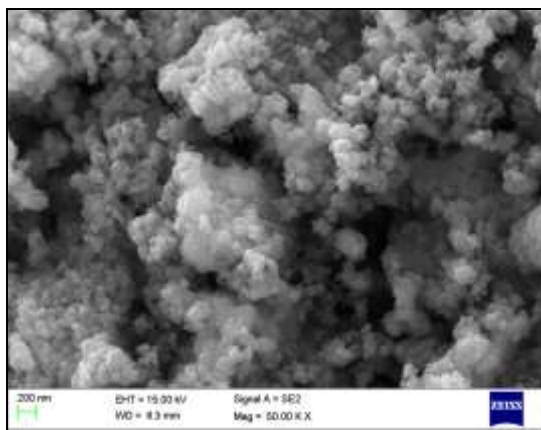
**Figure 2.8** (A)-(E) shows the SEM morphology of the as-synthesised spectra of the copper-cobalt ferrites of general formula  $\text{Cu}_{(1-x)}\text{Co}_x\text{Fe}_2\text{O}_4$  ( $x = 0, 0.25, 0.5, 0.75$  and  $1$ ) sintered at  $500\text{ }^\circ\text{C}$ .



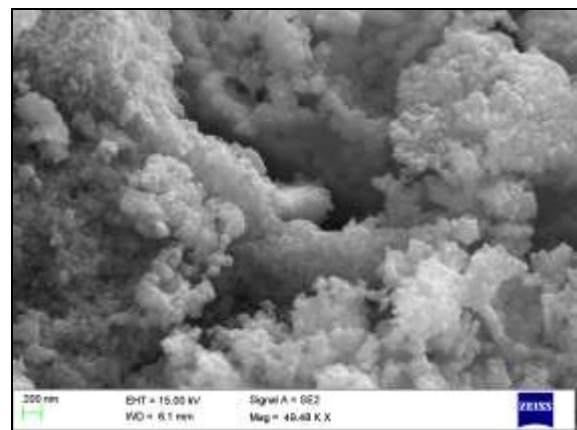
(A)  $\text{CuFe}_2\text{O}_4$



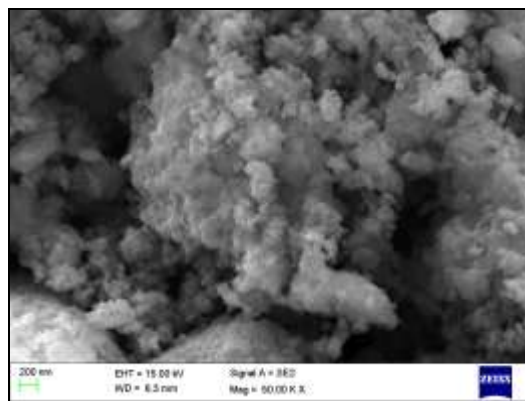
(B)  $\text{Cu}_{0.75}\text{Co}_{0.25}\text{Fe}_2\text{O}_4$



(C)  $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$



(D)  $\text{Cu}_{0.25}\text{Co}_{0.75}\text{Fe}_2\text{O}_4$



(E)  $\text{CoFe}_2\text{O}_4$

**Figure 2.8 (A)-(E) SEM images of copper-cobalt nano ferrites**

It can be seen from SEM micrographs of various compositions that the morphology of the particles is similar. They reveal largely agglomerated, well defined nano particles of the sample powder with in homogeneous broader grain size distribution. Such broader size distribution is characteristic of mechanically activated nano sized particles. The agglomeration of particles is also because they experience a permanent magnetic moment proportional to their volume. The micrographs give the appearance of a sponge structure with a large number of pores and this might be due to the fact that the copper is immiscible with cobalt.

### **2.3.4 Energy Dispersive Analysis of X-rays**

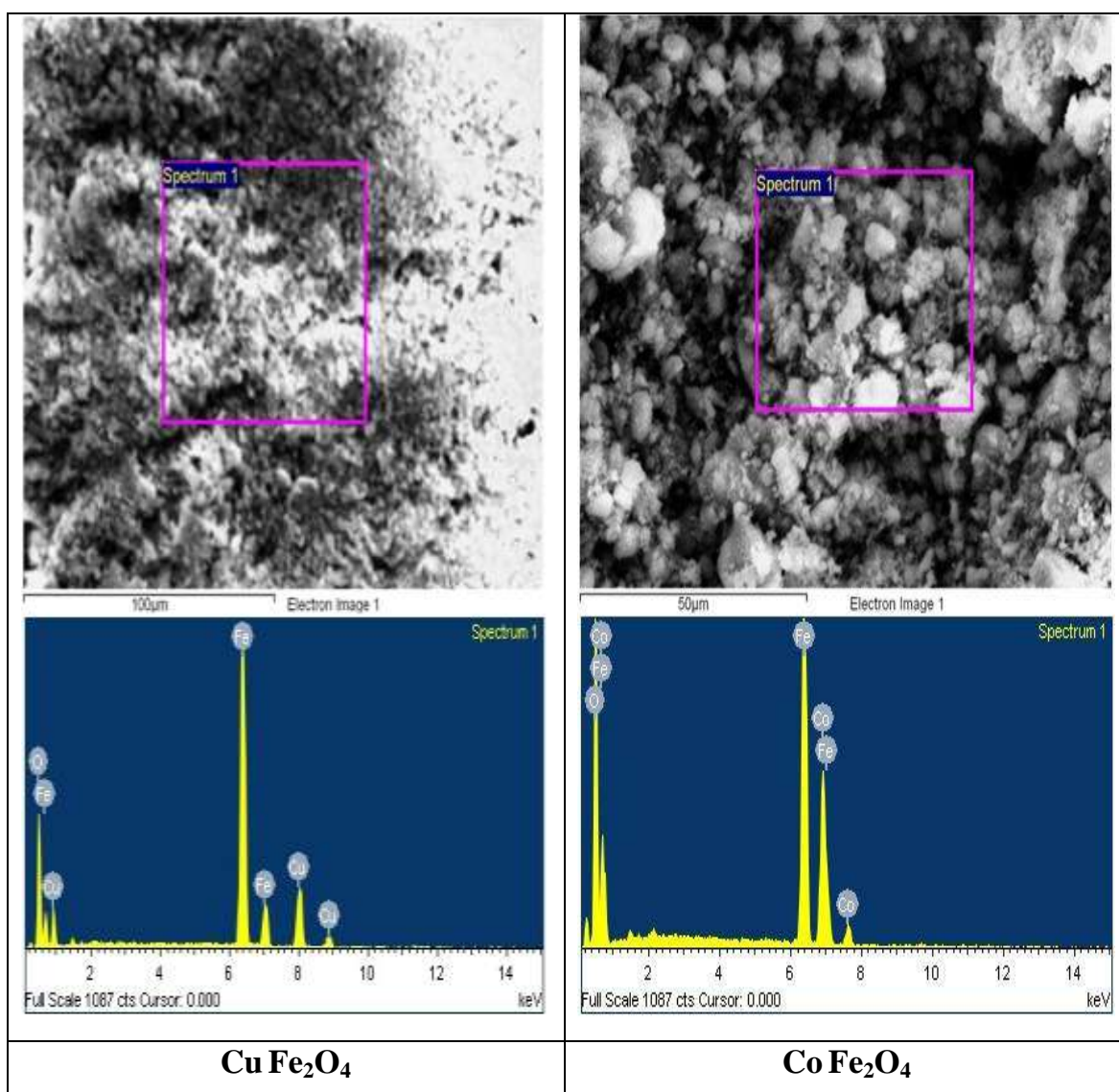
The high temperature calcination during the synthesis process may results in loss of ingredients that lead to non-stoichiometric composition. Such compositions show un-expected and unusual properties that cannot be explained on the basis of normal stoichiometry. Thus, it is essential to check the chemical stoichiometry of each synthesized composition before any further characterizations. Energy Dispersive Analysis of X-rays (EDAX) is an important tool for this purpose. The representative EDAX analysis of copper and cobalt ferrites (**Figure 9**) clearly reveals the presence of iron, copper, oxygen in copper ferrite and iron, cobalt and oxygen in cobalt ferrite samples and their purity.

### **Particle Distribution Analysis by TEM**

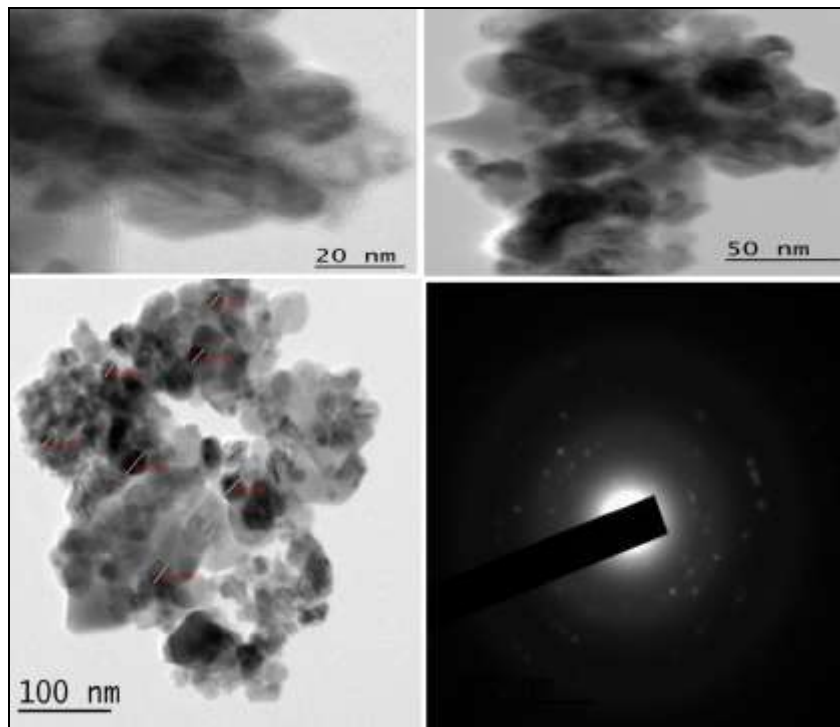
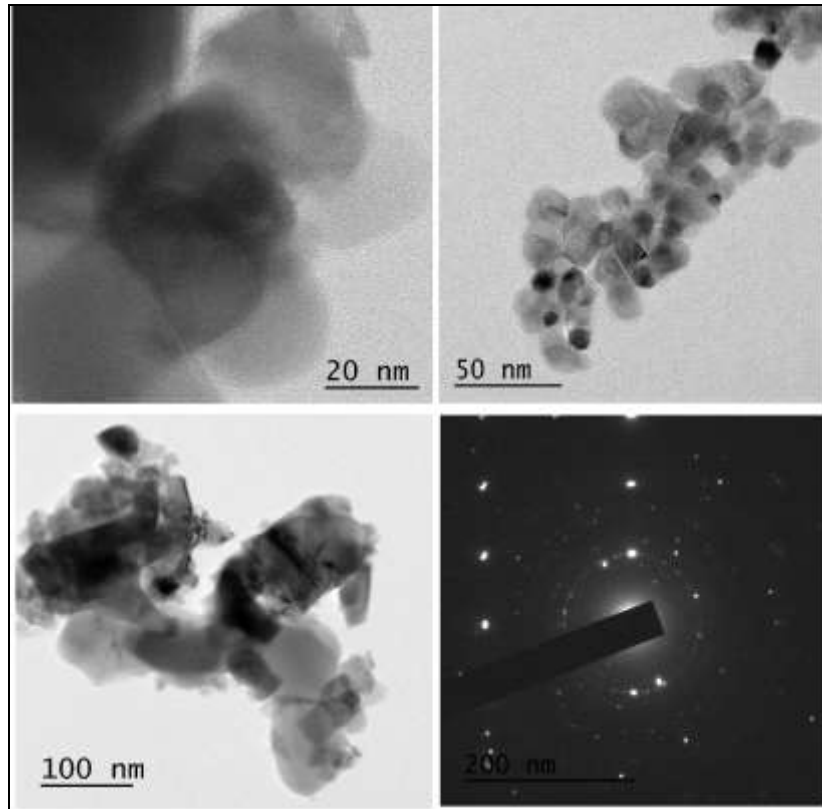
The representative TEM images of copper and cobalt ferrites are given in **Figures 10 (A) – (B)** shows the particle size distribution. The particles are irregular in shape and the major portions of the particles are in the size range of 30-40 nm. There is an element of agglomeration in the particles as seen the images.

The images illustrate the nano scale nature of ferrite particles. Agglomerated particles as well as separated ones are present in the sample. Mainly the nano particles tend to agglomerate because they experience a permanent magnetic moment proportional to their volume. Hence, each particle is permanently magnetized and gets agglomerated. The agglomeration can also be attributed, to a minor extent, to electrostatic or Vander Walls forces between

particles. The image also shows that the particles are mostly in the 30-40 nm size range, which collaborates well with the XRD investigation. The shape of the majority of the nano particles appears irregular. The SAED pattern reveals that the particles have high crystallinity. Each ring corresponds to the lattice parameter obtained in the XRD.



**Figure 9 EDAX images of  $\text{CuFe}_2\text{O}_4$  and  $\text{CoFe}_2\text{O}_4$**



**Figure 10 TEM Images of  $\text{CuFe}_2\text{O}_4$  (A) and  $\text{CoFe}_2\text{O}_4$  (B)**



### BET surface area analysis

The Brunauer, Emmett and Teller (BET) method [60] has been adopted as a standard procedure for surface area determination of powdered catalysts.

**Table 3 BET Surface Area analysis of Copper-Cobalt ferrite Samples**

Ferrite	BET Surface Area m <sup>2</sup> /g
CuFe <sub>2</sub> O <sub>4</sub>	165
Cu <sub>0.75</sub> Co <sub>0.25</sub> Fe <sub>2</sub> O <sub>4</sub>	160
Cu <sub>0.5</sub> Co <sub>0.5</sub> Fe <sub>2</sub> O <sub>4</sub>	157
Cu <sub>0.25</sub> Co <sub>0.75</sub> Fe <sub>2</sub> O <sub>4</sub>	155
CoFe <sub>2</sub> O <sub>4</sub>	153

The BET surface area of the CuFe<sub>2</sub>O<sub>4</sub> and CoFe<sub>2</sub>O<sub>4</sub> are found to be 165 and 153 m<sup>2</sup>/g respectively. The difference in the surface area of the samples is attributed to the atomic sizes of copper and cobalt listed in **Table 3**.

Nano particles of copper-cobalt ferrites with the general formula Cu<sub>1-x</sub>Co<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> (x = 0, 0.25, 0.5, 0.75 and 1) have been synthesized by citrate precursor sol-gel method. The FT-IR spectra show the absorption band around 575 cm<sup>-1</sup> which is attributed to the stretching vibrations of tetrahedral complexes and it shifts to lower values on doping with copper. The band around 410 cm<sup>-1</sup> is attributed to the stretching vibrations of octahedral complexes and it shifts to lower values upon increasing the concentration of cobalt ions. The XRD spectra reveal the average crystallite size to be in the range 30-40 nm and this is found to be in agreement with TEM results. The particle size is observed to increase with increase in cobalt concentration. The lattice parameter increases on inclusion of cobalt content. The SEM micrographs show the appearance of a sponge like structure. The EDAX spectra confirm the presence of metallic compounds without impurities.

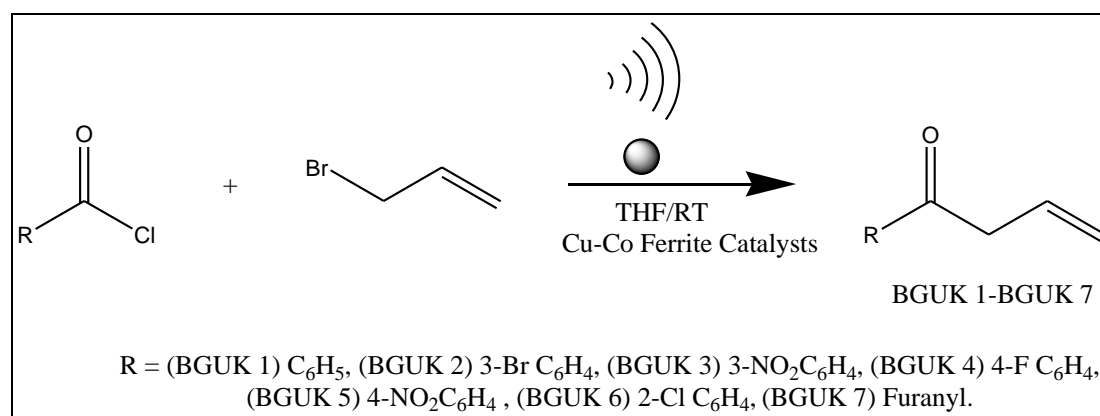


## Applications:

### Nano Copper-Cobalt Ferrite Catalyzed One-Pot Green Synthesis of $\beta, \gamma$ Unsaturated Ketones by Ultrasonication Method.

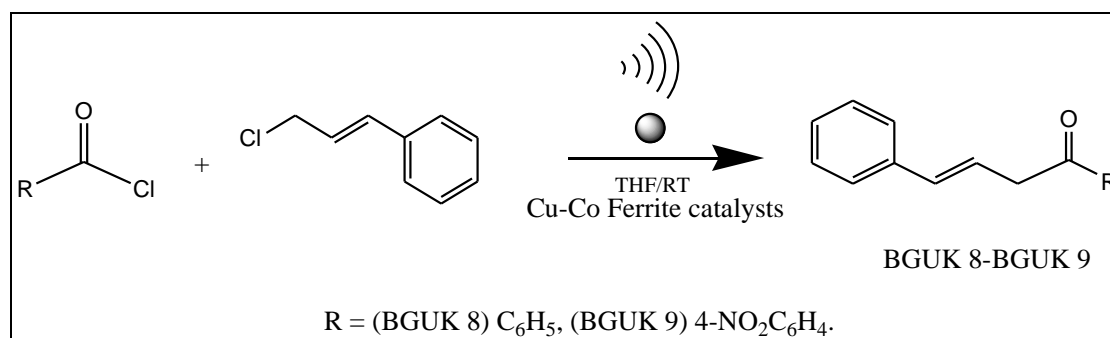
This chapter deals with the application of copper-cobalt ferrites in the one pot synthesis of pyridine derivatives, role of catalyst, plausible mechanism and process optimisation.

One-pot synthesis of substituted  $\beta, \gamma$ -unsaturated Ketones was carried over different spinel systems under study at a THF/RT where a mixture of allyl bromide (1 mmol) or cinnamyl chloride (1 mmol) and benzoyl chloride (1 mmol) were ultrasonicated in ethanol as shown below. The yield of  $\beta, \gamma$ -unsaturated Ketones formation with variation in copper-cobalt ratio is presented.



#### One-pot synthesis of $\beta, \gamma$ -unsaturated ketones with allylbromide

The results with allyl bromide have been extended with cinnamyl chloride. The synthetic route is presented below and the reaction was carried out under optimized conditions.

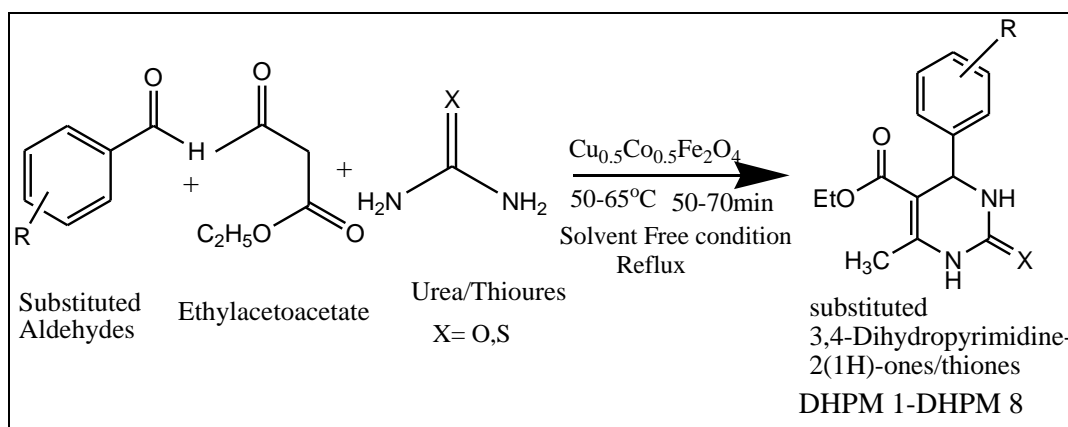


#### Synthesis of $\beta, \gamma$ -unsaturated ketones using cinnamyl chloride

### Copper-Cobalt Ferrite Catalyzed One Pot Synthesis Of 3,4-dihydro-

**pyrimidine-2(1H)-ones/thiones under solvent free conditions:** This chapter deals with the application of copper-cobalt ferrites in the one pot synthesis of 3,4-dihydro-pyrimidine-2(1H)-ones/thiones under solvent free conditions, role of catalyst, plausible mechanism and process optimisation.

A one-pot multi-component reaction of aldehydes, ethylacetoacetate and urea or thiourea is described for the preparation of 3,4-dihydropyrimidine- 2(1H) ones/ thiones using as cobalt substituted copper nano ferrites catalysts as a mild, inexpensive, and highly efficient catalyst. The effect of substrate as well as substituent as a catalyst in one-pot ,three-component Biginelli reaction in under solvent free condition between aldehydes, ethylacetoacetate and urea/thiourea synthesis of DHPMs. Approach for simple one pot Biginelli was a remarkable performance (> 90) of 3,4-dihydropyrimidine- 2(1H) ones/thiones shorter reaction time ( 50-70 min) versus the reaction time required for other catalyst. The key features of this methodology are operational simplicity, mild reaction conditions with good yields.

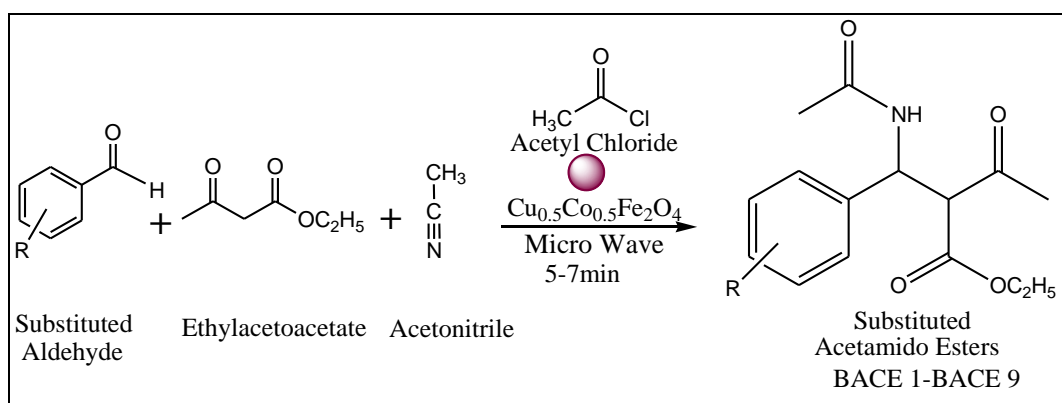


### One-pot synthesis of 3, 4 –Dihydropyrimidin-2(1H)-ones/ -thiones

#### Copper Cobalt Ferrite Catalysed Green One pot Synthesis of $\beta$ -Acetamido Esters:

This chapter deals with the application of copper-cobalt ferrites in the one pot synthesis of  $\beta$ -Acetamido Esters under microwave irradiation, role of catalyst, plausible mechanism and process optimisation.

One-pot synthesis of substituted  $\beta$ -Acetamido esters was carried out by the condensation of aldehydes, ethyl acetoacetate and acetonitrile (carrying both electron-donating and electron-withdrawing groups of aldehydes) in presence of  $\text{Cu}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$  as nano catalysts under Microwave condition as shown in below. The yield  $\beta$ -Acetamido esters formation with variation in copper-cobalt ratio is presented.

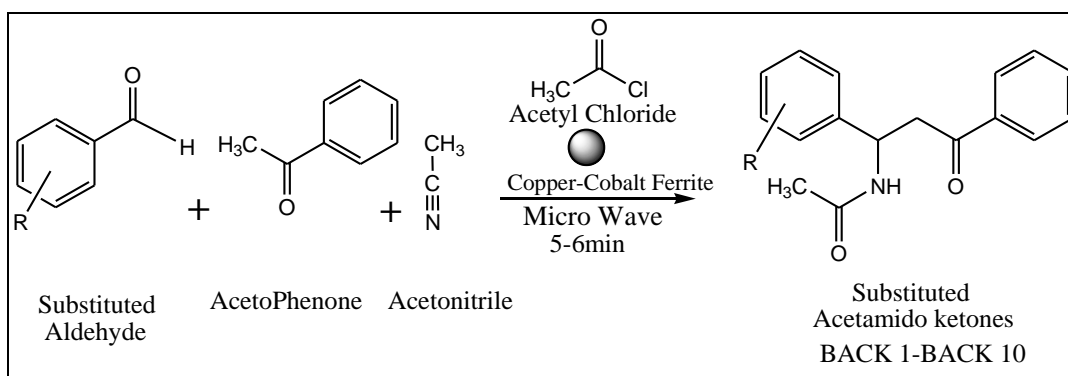


### One-pot synthesis of $\beta$ -acetamido Esters

#### Copper Cobalt Ferrite Catalysed Green One pot Synthesis of $\beta$ -Acetamido Ketones:

This chapter deals with the application of copper-cobalt ferrites in the one pot synthesis of  $\beta$ -Acetamido Ketones under microwave conditions, role of catalyst, plausible mechanism and process optimisation.

A one-pot multi-component reaction of aldehydes, enolizable ketones or 1,3-dicarbonyls, acetonitrile/ benzonitrile and acetyl chloride is described for the preparation of  $\beta$ -acetamido ketones using as cobalt substituted copper nano ferrite catalysts a mild, inexpensive and highly efficient catalyst.



### **One-pot synthesis of $\beta$ -acetamido ketones**

All the above schemes have been presented with the role of catalysts by suggesting the plausible mechanisms. It is further compared with the nature of the catalyst and also the method of reaction i.e. reflux/ ultrasonication/ microwave.

The efficiency of the catalyst is compared with the reported literature and it is found that these copper-cobalt nano ferrites have found to be excellent catalysts for the selected schemes of the reactions.

A number of compounds have been synthesized and their structures have been assigned with the help of FT-IR,  $^1\text{H}$  NMR and MASS spectral analysis. The supporting spectra are also provided.

### **Antibacterial Activity of the Heterocyclic Compounds Synthesised:**

In this chapter antibacterial activity studies of all the heterocyclic compounds synthesised by various synthetic strategies using nano copper-cobalt ferrites are presented

And finally fifteen samples of one-pot synthesized compounds were screened for their antibacterial activity on gram positive (*Bacillus subtilis*, *Staphylococcus aureus*) and gram negative bacteria (*Salmonella typhi*, *Enterobacter aerogenes*). Out of these 15 compounds DHPM 3, DHPM 4 did not show zone of inhibition for *Bacillus subtilis*, BACK 9 did not show zone of inhibition for *Staphylococcus aureus*. For gram negative bacteria, all compounds showed zone of inhibition from moderate to high in comparison with the standard drug.

### **Conclusions**

The summary of the work presented and the final conclusions of the work carried out.

Catalyst reusability is of major concern in heterogeneous catalysis. The recovery and reusability of the catalyst was investigated. Catalyst recycling was achieved by fixing the catalyst magnetically at the bottom of the flask with a strong magnet, after which the solution was taken off with a pipette, the solid washed twice with acetone and ethyl alcohol and the fresh substrate dissolved in

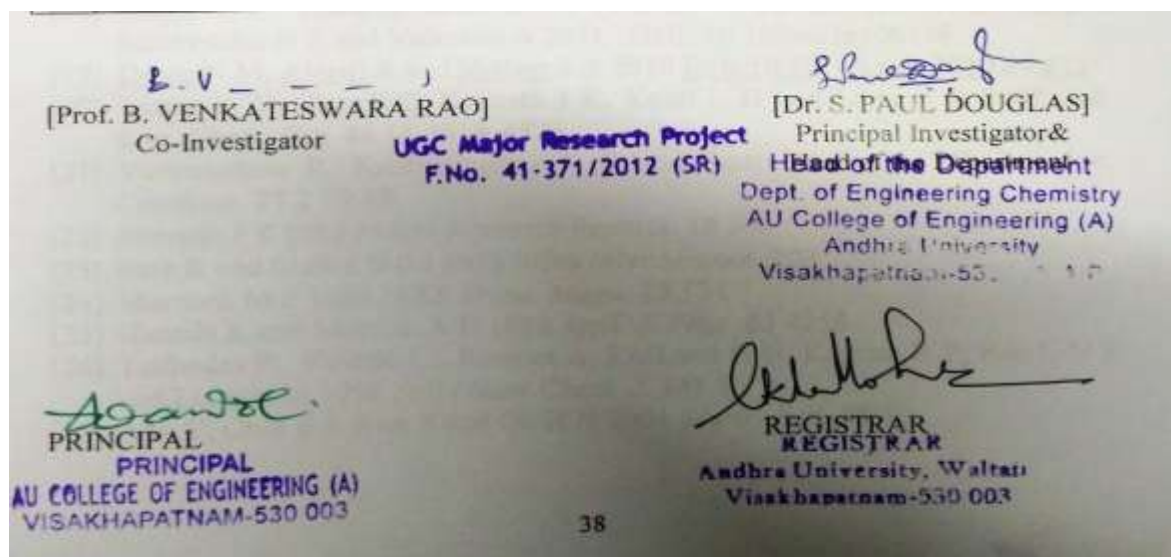
the same solvent was introduced into the flask, allowing the reaction to proceed for next run. The catalyst was consecutively reused five times without any noticeable loss of its catalytic activity. Therefore, they could be easily and almost completely separated by an external magnet which is of a great advantage for a heterogeneous catalyst.

It is concluded that efficient methods have been developed for the synthesis of  $\beta,\gamma$ -unsaturated ketones, 3,4-dihydropyrimidine- 2(1H) ones/ thiones,  $\beta$ -acetamido esters and  $\beta$ -acetamido ketones using nano copper-cobalt ferrites under reflux/ ultrasonication/ microwave methods. These methods offer several advantages including high yield, short reaction time and ease of separation and recyclability of the magnetic nano catalysts. The compounds are screened for their biological activity.

14.	Contributions to the Society	:	The results have been incorporated in many other studies
15.	Whether any Ph.D enrolled/produced out of the project:	:	<b>YES</b> Project Fellow Mr. Bassa Satyanaryana Enrolled as PhD Research Scholar Completed his course work and Submitted his Thesis He has been awarded PhD in Chemistry from Andhra University on the TOPIC <i>"Synthesis, Characterisation and Catalytic Applications of Nano Copper-Cobalt Ferrites"</i> <i>PhD Degree Proceedings Enclosed</i>
16.	No. of publications out of the project:	:	<b>13</b> Research papers were published.
<p><b>International Conference:</b> Paper Accepted for Presentation at 6<sup>th</sup> International Conference on Nano Science and Technology – ICONSAT-2014 Sponsored by Nano Mission, Dept. of Science and Technology, Govt. of India during 3-5 March 2014 – at INST, Chandigarh Theme: <b>Nano Catalysis</b> Title: <b>Nano Copper-Cobalt Ferrites as Magnetically Separable Catalysts for the One-pot Synthesis of 2,4,5-Tri Substituted Imidazoles</b></p>			

S. No	Title of the Publication, Authors, Journal	Year
1	A Novel Synthesis of Tellurium Nanoparticles using Iron(II) as a Reductant Vijaya Raju Kurimella, K. Raj Kumar and <b>Paul Douglas Sanasi*</b> International Journal of Nano Science and Nanotechnology; VoL 4 (3) <b>2013</b> pp. 209-221 ISSN 0974-3081	2013
2	A Novel Synthesis of Selenium Nanoparticles Vijaya Raju Kurimella, <b>Paul Douglas Sanasi</b> and Venkateswara Rao Battula International Journal of Nano Science and Nanotechnology – 4(1), <b>2013</b> , pp. 61-70 ISSN-0974-3081	2013
3	Nano copper and cobalt ferrites as heterogeneous catalysts for the one-pot synthesis of 2,4,5-tri substituted imidazoles <b>Paul Douglas Sanasi</b> , D Santhipriya, Y Ramesh, M Ravi Kumar, B Swathi and K Jaya Rao J. Chem. Sci. <b>2014</b> , 126 (6), 1715–1720. ISSN: 0973-7103 <a href="http://dx.doi.org/10.1007/s12039-014-0729-2">http://dx.doi.org/10.1007/s12039-014-0729-2</a>	2014
4	Microwave Assisted, Nickel-cobalt Ferrite Catalysed One-pot Multicomponent Synthesis of $\beta$ -Acetamido Ketones <b>Paul Douglas Sanasi</b> , Pandu Naidu Chilla, Ramesh Yellapragada, Satyanarayana Bassa, Ravi Kumar Majji, Swathi Bandaru, Rajendra Kumar Jeldi, Sruthi Vasamsetty International Journal of Engineering Science and Technology (IJEST) Vol. 7 No.12 Dec 2015 418-425 ISSN : 0975-5462	2015
5	Nano Copper Ferrite Catalyzed Sonochemical, One-Pot Three and Four Component Synthesis of Poly Substituted Imidazoles <b>Paul D. Sanasi</b> , Ravi K. Majji, Swathi Bandaru, Satyanarayana Bassa, Surekha Pinninti, Sruthi Vasamsetty, Raghu B. Korupolu Modern Research in Catalysis, January 2016, 5, 31-44 <a href="http://dx.doi.org/10.4236/mrc.2016.51004">http://dx.doi.org/10.4236/mrc.2016.51004</a>	2016
6	Magnetic Nano Cobalt Ferrite Catalyzed Synthesis of 4H-Pyrano[3,2-h]quinoline Derivatives under Microwave Irradiation Swathi Bandaru, Ravi K. Majji, Satyanarayana Bassa, Pandu N. Chilla, Ramesh Yellapragada, Sruthi Vasamsetty, Rajendra K. Jeldi, Raghu B. Korupolu, <b>Paul D. Sanasi</b> ; Green and Sustainable Chemistry, May 2016, 6, 101-109 <a href="http://dx.doi.org/10.4236/gsc.2016.62009">http://dx.doi.org/10.4236/gsc.2016.62009</a>	2016
7	Nano Copper Ferrite Catalysed Improved Procedure for One-Pot Synthesis of Poly Substituted Pyridine Derivatives <b>S. Paul Douglas</b> , B. Swathi, M. Ravi Kumar, Y. Ramesh, K. Jaya Rao, B. Satyanarayana and CH. Pandu Naidu Chemical Science Transactions 2016, <b>5(2)</b> DOI:10.7598/cst2016.1203; ISSN:2278-3458	2016
8	Nano Copper Ferrite Catalyzed Onepot Synthesis and Microbial Studies of Chalcone Derivatives A.Satheesh, H.Usha, M.Visalakshi, T.Rambabu, Ch.V.V.Srinivas, Y.Vamsi Kumar, <b>S. Paul Douglas</b> International Journal of Engineering Research & Technology (IJERT) ISSN: 2278-0181 Vol. 6 Issue 05, May - 2017	2017

S. No	Title of the Publication, Authors, Journal	Year
9	Catalyst Free One-Pot Synthesis of Chromeno Quinolines and Their Antibacterial Activity Sruthi Vasamsetty, Sunitha Medidi, Satheesh Ampolu, Ravi Kumar Majji, Mastan Rao Kotupalli, Chikurumilli China Satyanarayana, Annapurna Nowduri, Paul Douglas Sanasi Green and Sustainable Chemistry, 2017, 7, 141-151 <a href="https://doi.org/10.4236/gsc.2017.72011">https://doi.org/10.4236/gsc.2017.72011</a>	2017
10	Greener One-pot Synthesis of Hexahydroquinazolin-2(1H)-one/thione Derivatives and their Biological Activity Vamsi Kumar Y, Raghu Babu K, Satheesh A, Usha H, Chalapathi Rao Ch V, <b>Paul Douglas S</b> International Journal for Research in Applied Science & Engineering Technology (IJRASET) ISSN: 2321-9653; IC 6 (II), February 2018	2018
11	Visible Light Photocatalytic Degradation of Methylene Blue and Malachite Green Dyes with CuWO <sub>4</sub> -GO Nano Composite Sunitha Medidi, Sowmyasree Markapurapu, Mastan Rao Kotupalli, Rama Krishna Reddy Chinnam, Venkata Mahalakshmi Susarla, Hima Bindu Gandham1, <b>Paul Douglas Sanasi</b> Modern Research in Catalysis, 2018, 7, 17-34	2018
12	Visible Light Photocatalytic Degradation of Methylene Blue and Malachite Green Dyes with BaWO <sub>4</sub> -GO Nano Composite M. Sunitha, R. Soma Sekhar, B.Ravali, Ch. Rama Krishna Reddy, S.V. Mahalakshmi, V.Sruthi, <b>S. Paul Douglas</b> , International Journal of Environment, Agriculture and Biotechnology (IJEAB) 2(3), May-Jun- 2017 <a href="http://dx.doi.org/10.22161/ijeab/2.3.22">http://dx.doi.org/10.22161/ijeab/2.3.22</a> ISSN: 2456-1878	2018
13	Synthesis, Characterization and Visible Light Photocatalytic Degradation Study of Thiourea modified Nano Titania Composites Venkata Mahalakshmi Susarla, Somasekhar Ryali, Sunitha Medidi, Rama Krishna Reddy Chinnam and <b>Paul Douglas Sanasi</b> , Journal of Applicable Chemistry ISSN: 2278-1862 2018, 7 (2):325-334	2018



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# ANDHRA UNIVERSITY

Visakhapatnam - 530 003, Andhra Pradesh, INDIA  
NAAC - Accredited "A" Grade with a CGPA of 3.60 out of Four Point Scale  
"ISO 9001: 2015 Certified"

**Prof. V. KRISHNA MOHAN**  
M Com., M B A., Ph.D., FDPM (IIM-A)  
REGISTRAR



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Mobile: +91-98482 89827  
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e-mail: registrar@andhrauniversity.edu.in

No.U3/UC&SE/ Engg. Chem/2019-20

Date: 03.12.2019

To  
The Secretary  
University Grants Commission(MRP)  
Bahadur Shah Zafar Marg  
NEW DELHI 110 002

Sir,

Sub: Prof. S. Paul Douglas, Principal Investigator, Department of Engineering Chemistry,  
College of Engg, A.U. - Audited UC, SE & Refund of unspent amount - sending -  
Regarding.

Ref: Letter No. F. 41-371/2012(SR), dt: 09.06.2015 of UGC, New Delhi.

\*\*\*

I am herewith forwarding the Utilization Certificate, Statement of Expenditure and Travel / Field work, together with final report of the Project for a period of 3 years from 01.07.2012 to 30.06.2015 under the scheme of UGC Major Research Project entitled "Development and Characterisation of nano mixed oxides containing copper acrobat and Iron and study of their catalytic activity" in respect of Prof. S. Paul Douglas, Principal Investigator, Department of Engineering Chemistry, College of Engg, A.U Dept. of Engineering Chemistry, College of Engg, A.U.

Further, the available unspent balance of Rs. 2,43,463/- refunded to the Secretary, UGC, New Delhi by way of Demand Draft vide No. 273133 Dt: 02.12.2019 for kind information and necessary action.

Thanking you,

Yours faithfully,

  
(V. KRISHNA MOHAN)

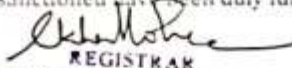
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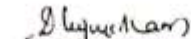
UNIVERSITY GRANTS COMMISSION  
BAHADUR SHAH ZAFAR MARG  
NEW DELHI - 110002


**UTILIZATION CERTIFICATE**  
**For the Period 01/07/2012 to 31/12/2015**

Certified that an amount of Rs. 14,77,800/- (Rupees Fourteen Lakhs Seventy Seven Thousand Eight Hundred Only) was sanctioned from University Grants Commission under the scheme of support for Major Research Project entitled "Development and Characterisation of nano mixed oxides containing copper cobalt and Iron and study of their Catalytic activity" vide UGC Letter No. F. No. 41-371/2012(SR) dated 16/07/2012 by the University grants commission. Out of the said grant a sum of Rs. 9,48,800/- (Rupees Nine Lakhs Forty eight Thousand Eight Hundred Only) released as first installment and Rs. 3,42,839/- (Rupees Three Lakhs Forty Two Thousand Eight Hundred and Thirty Nine ) totaling to Rs. 12,91,639/- (Rupees Twelve Lakhs Ninety One Thousand Six Hundred and Thirty Nine ) out of which Rs. 10,48,176/- (Rupees Ten Lakhs Forty Eight Thousand One Hundred and Seventy Six) has been fully utilized for the purpose for which it was sanctioned and in accordance with the terms and conditions laid down by University Grants Commission, and the unutilized amount of Rs.2,43,463/- (Rupees Two Lakh Forty Three Thousand Four Hundred and Sixty Three) should be returned to the University Grants Commission, New Delhi.

Certified that I have satisfied myself that the conditions on which the grants-in-aid were sanctioned have been duly fulfilled.

  
REGISTRAR  
Andhra University, Waltair  
Visakhapatnam-530 003  
Registrar with Seal

  
Finance Officer  
Andhra University  
Finance Officer with seal

  
Dr. S. PAUL DOUGLAS  
Associate Professor  
Dept. of Engg. Chemistry  
A.U. College of Engg. (A)  
Andhra University  
Visakhapatnam-530 003  
Principal Investigator  
UGC Major Research Project  
F.No. 41-371/2012 (SR)

For Rao & Kumar  
Chartered Accountants  
Firm Reg.No.003089S

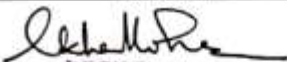
  
CA C.M. Ravi Prasad  
(Partner)

(M.No. 211322)

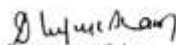

UDIN: 1921322AARAEW444

UNIVERSITY GRANTS COMMISSION  
DEPARTMENT OF ENGINEERING CHEMISTRY, ANDHRA UNIVERSITY  
STATEMENT OF EXPENDITURE FOR THE PERIOD 01/07/2012 TO 30/06/2015

S.No. (I)	Sanctioned Heads (II)	Total Grant approved by the UGC (III)	Grant released by UGC as first Installment (IV)	Actual Expenditure Incurred 01/07/2012 to 30/06/2015 (V)	Balance as at 30/06/2015 IX = (V - VII)
<b>A</b>	<b>Non-Recurring Expenses:</b>				
1	Books & Journals	20,000.00	20,000.00	20,000.00	-
2	Equipment ( Microwave oven, sonicator, vacuum pump, electronic balance	3,00,000.00	3,00,000.00	2,99,969.00	31.00
	<b>Sub Total (A)</b>	<b>3,20,000.00</b>	<b>3,20,000.00</b>	<b>3,19,969.00</b>	<b>31.00</b>
<b>B</b>	<b>Recurring Expenses:</b>				
1	Project Fellow	5,28,000.00	2,64,000.00	2,62,700.00	1,300.00
2	Chemicals/Glassware/Consumables	2,70,000.00	1,35,000.00	1,34,859.00	141.00
3	Hiring Services	1,00,000.00	50,000.00	50,000.00	-
4	Contingency	1,00,000.00	50,000.00	50,000.00	-
5	Travel/Field Work	60,000.00	30,000.00	30,000.00	-
6	Overheads Charges	99,800.00	99,800.00	99,800.00	-
	<b>Sub Total (B)</b>	<b>11,57,800.00</b>	<b>6,28,800.00</b>	<b>6,27,359.00</b>	<b>1,441.00</b>
	<b>Total (A+B)</b>	<b>14,77,800.00</b>	<b>9,48,800.00</b>	<b>9,47,328.00</b>	<b>1,472.00</b>

  
REGISTRAR  
Andhra University, Waltair  
Visakhapatnam  
Registrar with Seal

  
Signature of the  
Principal Investigator  
UGC Major Research Project  
F.No. 41-371/2012 (SR)

  
Signature of the  
Finance officer with seal  
Finance Officer  
Andhra University  
Visakhapatnam  
For Rao & Kumar  
Chartered Accountants  
Firm Reg.No.0030895  
  
CA C.M. Ravi Prasad  
(Partner)  
(M.No. 211322)



UDIN :- 19211322AAAAE V5697




**UNIVERSITY GRANTS COMMISSION, BAHADURSHAH JAFAR MARG, NEW DELHI 110002**  
**STATEMENT OF EXPENDITURE INCURRED ON HIRING SERVICES**  
**UGC-MRP-F.NO.41-371/2012(SR) PRINCIPAL INVESTIGATOR: DR. S. PAUL DOUGLAS**

STATEMENT OF EXPENDITURE - HIRING SERVICES					
S. No	Particulars	Bill No.	Date	Firm	Amount
	Advance Received from the Registrar, AU	Cheque, AU	5/10/2012		50000
1	Antibacterial and antifungal activities	1254	18/12/2012	TRIMS, Pvt Ltd	4000
2	XRD Analysis Charges	77	8/8/2013	Advanced Analytical Laboratory, DST Purse, AU	1800
3	NMR Charges 10 Samples@300	307	4/9/2013	Chem Anal Synth Solutions, VSP	3000
4	FT-IR Charges 10 samples@100	308	4/9/2013	Chem Anal Synth Solutions, VSP	1000
5	Mass Charges 10 samples @400	310	4/9/2013	Chem Anal Synth Solutions, VSP	4000
6	NMR Charges 10 Samples@300	312	5/1/2014	Chem Anal Synth Solutions, VSP	3000
7	FT-IR Charges 10 samples@100	313	5/1/2014	Chem Anal Synth Solutions, VSP	1000
8	Mass Charges 10 samples @400	314	5/1/2014	Chem Anal Synth Solutions, VSP	4000
9	NMR Charges 10 Samples@300	321	18/1/2014	Chem Anal Synth Solutions, VSP	3000
10	FT-IR Charges 10 samples@100	322	18/1/2014	Chem Anal Synth Solutions, VSP	1000
11	Mass Charges 10 samples @400	323	18/1/2014	Chem Anal Synth Solutions, VSP	4000
12	NMR Charges 10 Samples@300	335	20/1/2014	Chem Anal Synth Solutions, VSP	3000
13	FT-IR Charges 10 samples@100	336	20/1/2014	Chem Anal Synth Solutions, VSP	1000
14	Mass Charges 8 samples @400	337	20/1/2014	Chem Anal Synth Solutions, VSP	3200
15	Antimicrobial Activity	1221	22/2/2014	TRIMS, Pvt Ltd	10000
16	Anticancer Activity	1233	4/3/2014	TRIMS, Pvt Ltd	3000
				<b>Total Expenditure</b>	<b>50000</b>

Advance Received from the Registrar, AU  
 Total Expenditure  
 Balance

50000  
 50000  
 0

  
 Principal Investigator  
 Principal Investigator  
 UGC Major Research Project  
 F.No. 41-371/2012 (SR)

  
 FOR RAO & KUMAR  
 CHARTERED ACCOUNTANTS  
 FIRM REG. NO. 0030895



  
 REGISTRAR  
 Andhra University, Waltair  
 Visakhapatnam-530 003

C.P. 11/19/2014  
 18/01/2014


UNIVERSITY GRANTS COMMISSION, BAHADURSHAH JAFAR MARG, NEW DELHI 110002

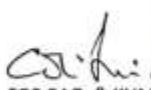
STATEMENT OF EXPENDITURE INCURRED ON CONTINGENCY

UGC-MRP-F.NO.41-371/2012(SR)

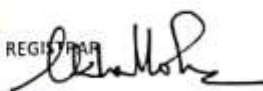
PRINCIPAL INVESTIGATOR: DR. S. PAUL DOUGLAS

S. No	Particulars	Bill No.	Date	Firm	Amount
	Advance Received from the Registrar		5/10/2012	Cheque, AU	50000
1	Attendance Register, Account Book, Stock Register	297	31/10/2012	Visalandhra Slate Industries	210.00
2	Files, A4 Paper, Folders, Registers	165	8/11/2012	Visalandhra Slate Industries	677.00
3	UPS Battery Replacement	561	12/11/2012	Sun Power Systems	650.00
4	Printer Toner Refilling and Drum	678	15/11/2012	Lalitha Enterprises	650.00
5	Paints, brushes and powders for racks	3640	27/08/2013	Sree Enterprises	3029.00
6	Painter Charges	Voucher	30/09/2013	Shirdi Sai Interiors	4000.00
7	Xerox	512	1/10/2013	Raj E-Net Center, Xerox	100.00
8	Electrical Fittings for the Equipment	632	31/10/2013	Lal Electricals	1150.00
9	Electrical Fittings for the Equipment	423	31/10/2013	Lal Electricals	2492.00
10	Electrician Charges	Voucher	10/11/2013	Shirdi Sai Interiors	1800.00
11	Xerox	6	14/11/2013	Gayatri Titanic Xerox	150.00
12	Xerox	77	16/11/2013	Gayatri Titanic Xerox	570.00
13	Mid Term Report Printing and Xerox	69	4/2/2014	Gayatri Titanic Xerox	240.00
14	Mid Term Report Binding	755	4/2/2014	SVR Pri&Binders	180.00
15	Heating Mantle	75	25/05/2014	Sri Sai Enterprises	3206.00
16	Magnetic Stirrer	93	26/06/2014	Sri Sai Enterprises	4809.00
17	Xerox	1	6/7/2014	Gayatri Titanic Xerox	49.00
18	Printer Toner Refilling	888	8/7/2014	Lalitha Enterprises	250.00
19	Research Chemicals	104	11/7/2014	Sri Sai Enterprises	4273.00
20	Xerox	18	3/8/2014	Gayatri Titanic Xerox	100.00
21	Xerox	35	4/8/2014	Gayatri Titanic Xerox	320.00
22	Research Chemicals	112	4/8/2014	Sri Sai Enterprises	3625.00
23	Hotplate Round	122	28/8/2014	Sri Sai Enterprises	2863.00
24	Electrical Equipment for Photocatalytic Experiment	1534	24/9/2014	Mercury Agencies	2136.00
25	Wooden Box for the Photocatalytic Experiment - Wood and Making Charges 27"x26"x13"	Voucher	27/9/2014	Shirdi Sai Interiors	4500.00
26	Research Chemicals	196	5/12/2014	Sri Sai Enterprises	3685.00
27	Research Chemicals	201	19/12/2014	Sri Sai Enterprises	4683.00
				<b>Bills Submitted</b>	<b>Total Expenditure</b>
				<b>Bills Limited-Advance Adjusted</b>	<b>50397.00</b>
					<b>50000.00</b>

  
Principal Investigator  
Principal Investigator  
UGC Major Research Project  
F.No. 41-371/2012 (SR)

  
FOR RAO & KUMAR  
CHARTERED ACCOUNTANTS  
FIRM REG. NO. 0030895

C.M. RAO PRASAD  
1/10/12  
REG. NO. 211222

  
REGISTRAR  
Andhra University, Vizag  
Vizakhapatnam-512 003

**UNIVERSITY GRANTS COMMISSION, BAHADURSHAH JAFAR MARG, NEW DELHI 110002**  
**STATEMENT OF EXPENDITURE INCURRED ON FIELD WORK**  
**PRINCIPAL INVESTIGATOR: DR. S. PAUL DOUGLAS**

**UGC-MRP-F.NO.41-371/2012(SR)**

S. No	Name of the Person Travelled	Particulars of Travel for Research Project Purpose	Mode of Travel	Date	TICKET/ PNR NO	Amount
		Advance Received from the Registrar		5/10/2012	Opening Balance	
1	Dr. S. Paul Douglas Principal Investigator	Travel to IICT & Osmania University Hyderabad for catalyst preparation and characterisation				
		VSKP to Secunderabad 3A TRAIN	Train	3/1/2013	6432453256	655.00
		Secunderabad to VSKP 3A TRAIN	Train	11/1/2013	4272564528	655.00
2	Dr. S. Paul Douglas Principal Investigator	Travel to IICT & Osmania University Hyderabad for Sample Analysis				
		VSKP to Secunderabad 3A TRAIN	Train	8/2/2013	6514245869	655.00
		Secunderabad to VSKP 3A TRAIN	Train	10/2/2013	4351247568	655.00
3	Dr. S. Paul Douglas & B. Satyanarayana	Travel to IICT & Osmania University Hyderabad for Sample Analysis				
		VSKP to Secunderabad 3A TRAIN	Train	3/5/2013	6248751432	1310.00
		Secunderabad to VSKP 3A TRAIN	Train	10/5/2013	4856926355	1310.00
4	Mr. B. Satyanarayana Project Fellow	Travel to IICT & Osmania University Hyderabad for Sample Analysis				
		VSKP to Secunderabad 3A TRAIN	Train	21/5/2013	6547184522	655.00
		Secunderabad to VSKP 3A TRAIN	Train	25/5/2013	4257158699	655.00
5	Dr. S. Paul Douglas Principal Investigator	Travel to IICT & Osmania University Hyderabad for Sample Analysis				
		VSKP to Secunderabad 3A TRAIN	Train	30/06/2013	6320859353	655.00
		Secunderabad to VSKP 3A TRAIN	Train	2/7/2013	4806319234	655.00
6	Dr. S. Paul Douglas Principal Investigator	Travel to NIT Warangal for Experimental Work (Combined Ticket)				
		VSKP to Warangal 3A Train	Train	16/1/2014	6226155287	750.00
		Warangal to VSKP 3A Train	Train	18/1/2014	4258445728	570.00
7	Dr. S. Paul Douglas Principal Investigator	Travel to New Delhi for attending Mid Term Evaluation at UGC on 08.02.2014 to Dr. S. Paul Douglas, Principal Investigator (Combined Ticket)				
		VSKP to Delhi NZM - 3A Train	Train	6/2/2014	6723880490	1687.47
		Delhi NZM to VSKP - 3A Train	Train	9/2/2014	2154973468	1767.47
8	Prof. B. Venkateswara Rao Co-Investigator	Travel to INIST, Mohali and Panjab University to Prof. B. Venkateswara Rao [Co-Investigator]				



		VSKP to New Delhi - Flight Air India	Flight	2/3/2014	JY9NX	8974.00
		New Delhi to VSKP - Flight Air India	Flight	7/7/2014	JY9NX	
		New Delhi to Chandigarh - Train	Train	2/3/2014	2729143289	441.23
		Chandigarh to New Delhi - Train	Train	6/7/2014	2255581680	441.24
9	Mr. B. Satyanarayana Project Fellow	Travel to IIT - Bombay to Mr. Bassa Satyanarayana for Sample Analysis	Train	13/6/2014	6626808834	526.24
		Mumbai CST to VSKP	Train	17/6/2014	8511963534	526.24
10	Mr. B. Satyanarayana Project Fellow	Travel to SN Bose National Centre for Basic Science, Kolkata for Sample Analysis				
		VSKP to Howrah Jn	Train	20/12/2014	4823151075	471.24
11	Mr. B. Satyanarayana Project Fellow	Travel to IIT & Osmania University Hyderabad for Sample Analysis				
		VSKP to Secunderabad Train - Sleeper	Train	14/2/2015	6138004735	236.24
		Secunderabad To VSKP Train - Sleeper	Train	18/2/2015	4258692153	225.00
12	Dr. S. Paul Douglas Principal Investigator	Travel to IIT Hyderabad for Sample Analysis				
		VSKP to Secunderabad	Train	24/03/2015	6239297861	1239.94
		Secunderabad to VSKP	Train	26/03/2015	4106916415	1239.94
13	Dr. S. Paul Douglas Principal Investigator	Travel to IIT Hyderabad for Sample Analysis				
		VSKP to Secunderabad	Train	13/04/2015	613908104	1239.94
		Secunderabad to VSKP	Train	15/04/2015	4106916451	1239.94
14	Mr. B. Satyanarayana Project Fellow	Travel to IIT Delhi for Sample Analysis				
		Rajahmundry to H Nizamuddin	Train	10/4/2015	6639888894	742.47
15	Mr. B. Satyanarayana Project Fellow	Travel to IIT - Bombay to Mr. Bassa Satyanarayana for Sample Analysis				
		VSKP to Mumbai CST Train - Sleeper	Train	17/4/2015	6739238046	601.24
		Mumbai CST to RYJ Train - Sleeper	Train	19/4/2015	8234134197	551.24
		Bills Submitted - Total Expenditure				31326.08
		Bills Limited-Advance Adjusted				30000.00

  
**PRINCIPAL INVESTIGATOR**  
**Principal Investigator**  
**UGC Major Research Project**  
 T.No. 41-371/2012 (SR)

  
**FOR RAO & KUMAR CHARTERED ACCOUNTANTS**  
 FIRM REG. NO. 0030895 (A.R.)  
 Chartered Accountants

  
**REGISTRAR**

Andhra University, Waltair  
 Visakhapatnam-530 003

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e-mail: deanacademic.au@gmail.com



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should be addressed to the Dean by  
designation and not by the name

NOTIFICATION

AWARD OF RESEARCH DEGREE  
in

**CHEMISTRY**

It is hereby notified that the Vice-Chancellor on the recommendation of the Board of Examiners is pleased to order that **Mr. SATYANNARAYANA BASSA** be declared qualified for the **Degree of Doctor of Philosophy (Ph.D.) in CHEMISTRY** on the thesis entitled **"SYNTHESIS, CHARACTERISATION AND CATALYTIC APPLICATIONS OF NANO COPPER-COBALT FERRITES"**

(BY ORDER)

Central Administrative Office  
Visakhapatnam.  
Dt: **20-10-2017**

  
(T. V. SATYAVATHI DEVI)  
DEPUTY REGISTRAR (ACADEMIC)

Endt. No. **T(2)/8093/2016/P.T.**

Dt: **20-10-2017**

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NOTIFICATION

AWARD OF RESEARCH DEGREE  
 in

**CHEMISTRY**

It is hereby notified that the Vice-Chancellor having considered the reports of the following examiners appointed to adjudicate and report on the thesis entitled "**SYNTHESIS, CHARACTERISATION AND CATALYTIC APPLICATIONS OF NANO COPPER-COBALT FERRITES**"

01. **PROF. HUAN-JUNG FAN, HUNGKUANG UNIVERSITY, TAIWAN, R.O.C.**
02. **PROF. M.V. BASAVESWARA RAO, SPECIAL OFFICER, KRISHNA UNIVERSITY DR. MRAR PGC, NUZVID – 521 201, KRISHNA DISTRICT, A.P.**
03. **PROF. DR. G. VENKATESA PRABHU, DEPARTMENT OF CHEMISTRY, NIT, TIRUCHIRAPALLI – 620 015, T.N.**

On the recommendation of the following examiners who have conducted the Viva-Voce examination, the Vice-Chancellor is pleased to order that **Mr. SATYANNARAYANA BASSA** be declared qualified for the **Degree of Doctor of Philosophy (Ph.D.) in CHEMISTRY.**

- |                                       |   |   |
|---------------------------------------|---|---|
| 01. <b>PROF. K. RAGHU BABU</b>        | - | <b>D.C. MEMBER &amp; HEAD OF THE DEPARTMENT</b>                     |
| 02. <b>PROF. K. CHANDRA MOULI</b>     | - | <b>D.C. MEMBER</b>  |
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| 06. <b>PROF. B. VENKATESWARA RAO</b>  | - | <b>JOINT RESEARCH DIRECTOR &amp; D.R.C. MEMBER</b>                  |
| 07. <b>DR. PAUL DOUGLAS SANASI</b>    | - | <b>D.R.C. MEMBER, RESEARCH DIRECTOR &amp; CONVENER OF VIVA-VOCE</b> |

Date of submission of thesis : **21-10-2016**

( BY ORDER )

Central Administrative Office,  
 Visakhapatnam.

Dt: **20-10-2017**

(T. V. SATYAVATHI DEVI)  
 DEPUTY REGISTRAR (ACADEMIC)

Forwarded to the candidate **Mr. SATYANNARAYANA BASSA, S/O. B. SESHAGIRI, CHINNA SANKARAPUDI (P), PRATHIPADU (M.D), E.G. DIST., A.P., PIN 533432** with the information that out of the three copies of the thesis submitted by him/her one copy is retained for reference in the University Library and the remaining two copies will be given to him/her if the adjudicators returned them.

  
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