Title of the Project: **SYNTHESIS AND STUDIES ON PROPERTIES OF MIXED–METAL OXIDE SYSTEMS**

UGC APPROVAL LETTER NO. AND DATE:

F. No. 47-2038/11(WRO) dated **22.02.2012**

The progress has been according to original plan of work and towards achieving the objectives. There is a good scope for the investigation of mixed-metal oxides with reference to their structural properties. Principal Investigator desire to study the effect of synthetic method, structural parameters, particle size, electronic properties (band gap, thermo emf), magnetic properties, oxidation state, surface characterization (using ESCA) as well as electron microscopy of mixed–metal oxides on their performance. The different metal oxide systems $Zn_{1-x}Ni_xFeCrO_4$, $Mg_{1-x}Ni_xFeCrO_4$ and $Zn_{1-x}Cu_xFeCrO_4$ are prepared by a novel and facile gel combustion route. This wet chemical method overcome all drawbacks of conventional ceramic process and produce ultra-fine, homogeneous and reproducible ferrite powders using aqueous solutions of nitrate salts of constituent ions. The in situ oxidizing environment provided by the nitrate ions in the gel increases the rate of oxidation reaction and lowers the decomposition temperature of component, resulting in a self-propagating combustion. From X-ray analysis, all the system shows the formation of fcc type simple cubic structure with a thermal stability at high temperature. IR spectrum are found to exhibit two bands i.e. the absorption band ν_1 for stretching vibration of the tetrahedral M–O bands and the absorption band ν_2 for the M–O vibrations in octahedral site. Typical morphologies of the samples visualized by SEM, exhibit mainly an intergranular porosity and the absence of internal pores. It is found that Zn rich samples are small in size while Ni, Cu rich samples have cubic grains. EDS analysis at room temperature for the composition of the metals in system are found to be equal to the relative compositions of the metals used for synthesis by stoichiometric calculation. The results of resistivity measurements show the semiconducting nature of the compounds where decrease in resistivity was observed with increasing temperature due to increase in the thermally activated drift mobility of charge carriers on hopping. The temperature dependent Seebeck coefficient shows

both types of charge carriers take part in the conduction process. Appearance of super paramagnetic phase in Ni substituted samples of cubic spinel is main feature of the work.

The results and achievements from the work done in the project have been summarized in the following points.

1. Thermal analysis for all the precursors shows that decomposition occurs at or below 800^{o}C. Above which, the powders exhibits a constant weight. Hence all are thermally stable above this temperature.
2. EDS analysis of all the oxides shows, a good agreement between the experimental values and those expected theoretically. The observed composition is almost equal to that of the samples produced by stoichiometric calculations.
3. All the synthesized samples of the system, they show the fundamental peaks of single phase cubic spinel. The X-ray patterns were well indexed and a cubic lattice was observed belonging to the fcc system.
4. The oxides synthesized by the combustion method are highly porous. The grain size esteemed from the SEM photograph using Cottrel's method is consistent with the size calculated by Debye-Scherrer formula from the (311) peak of XRD patterns.
5. The room temperature infrared spectra are found to exhibit two bands in the range 400-600cm^{-1} which are the common features of all ferrites. The absorption band ν_1 is caused by the stretching vibration of the tetrahedral M-O bands, and the absorption band ν_2 is caused by the M-O vibrations in octahedral site.
6. In all samples, electrical resistivity decreases with increasing temperature indicating semiconducting nature and obeying Wilson's law.
7. Transport properties showed all the compounds to be semiconductors and the Seebeck coefficient are obtained from the slope of the plots.
8. The samples are used as a catalyst in three component condensation reaction which did not change its chemical composition and its structure after use. Hence the samples are reusable catalysts in organic reactions.

9. The photodecolourisation and degradation process of certain dyes over the systems gives an idea about photocatalytic activity of the systems. Hence the concentrations of dyes were successfully determined when the dyes are exposed to UV light in presence of synthesized photocatalyst.

CONTRIBUTION TO THE SOCIETY:

Spinels containing transition metal ions are of great commercial importance. The growth of chemical industry needs the availability of good catalytic system or an ability of an industry to synthesize new catalyst so that specific product having varied applications can be produced. Catalysts (both homogeneous and heterogeneous) play important role in the synthesis of about 80% of all chemicals. Photocatalytic oxidation is an economical process owing to the fact that it involves only a photocatalyst and light source. This process does not yield toxic intermediate product, making it suitable for cleaning water environment.

Dyes are the major pollutants from various industries such as textile, paper, plastic, leather, cosmetics etc. where they are used for coloring purpose. The effluent discharged by various textile industries contains a large number of dyes, increasing the total COD of wastewaters. These are toxic and hazardous to many organisms. Therefore effective removal of dyes from wastewater of these industries remains a challenge. Because of stringent government legislations, it is important to remove dyes from wastewater before they are contacted with unpolluted natural water.

The compounds thus synthesized by sol-gel processes has the advantages of inexpensive precursors, a simple preparation method, and a resulting nano-sized, homogeneous, highly reactive powder. The compounds are more effective catalysts as compared to pure oxides exhibiting variety of local site symmetries and thus are useful for various catalytic reactions in the industries and photo degradation and remediation of water effluents.

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