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## Structural, magnetic and gas sensing properties of nanosized copper ferrite powder synthesized by sol gel combustion technique

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## ABSTRACT

Stoichiometric nano sized copper ferrite particles were synthesized by sol gel combustion technique. They were then calcined at various temperatures ranging from 300–800 °C and were either furnace cooled or quenched in liquid nitrogen. A high magnetisation value of 48.2 emu/g signifying the cubic phase of copper ferrite, was obtained for sample quenched to liquid nitrogen temperature from 800 °C. The ethanol sensing response of the samples was studied and a maximum of 86% response was obtained for 500 ppm ethanol in the case of a furnace cooled sample calcined at 800 °C. The chemical sensing is seen to be correlated with the *c/a* ratio and is best in the case of tetragonal copper ferrite.

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## 1. Introduction

Recently, spinel ferrites are extensively studied for their potential use as chemical sensors, in their pure form, as mixtures and as spinel ferrite-metal oxide composite materials [1–4]. It is also known that many factors such as the chemical species, surface morphology, synthesis methods and operating temperature affects the chemical sensing response. There have been a few reports comparing the chemical sensing response of various ferrites. Rezliescu et al. [5] have compared the response of copper, cadmium and zinc ferrite and have shown that copper ferrite responds more towards reducing gases than the other two. The operating temperature of ferrites varies from 250 °C to 550 °C. It was shown earlier that copper ferrite detects ethanol at lower temperature of 290 °C, in comparison with nickel ferrite (550 °C) [6], magnesium ferrite (335 °C) [7] and cadmium ferrite 380 °C [8].

Among these ferrites, copper ferrite, is a mixed ferrite and is interesting because of its gas sensing and structural properties. The magnetisation values in copper ferrite are quite distinct, ~1700 G (25 emu/g for room temperature measurement of powder samples) for tetragonal and > 3000 G (44 emu/g) for the cubic phase [9,10]. In bulk it has a tetragonally distorted spinel structure when most Cu<sup>2+</sup> ions occupy the octahedral B site, in

which case this site occupancy also leads to Jahn Teller distortion, rendering the *c/a* ratio to be > 1 at room temperature. This transforms to the cubic phase above 350 °C. Additionally it is also known, in the case of bulk, that only high temperature quenching (from 1300 °C) results in the cubic phase. Magnetisation enhancement of copper ferrite by stabilizing the cubic phase at room temperature has been reported in thin films [9]. The magnetisation enhancement is possible if Cu<sup>2+</sup> ions from the octahedral site migrate to the tetrahedral site. This affects both the structure and magnetic properties. Since chemical sensing is normally ion specific, it was surmised that in the case of copper ferrite, thermal treatment may influence the cation site occupancy and thus the sensing performance.

The effect of thermal treatment on the magnetic properties of copper ferrite is well studied [11]. However, the effect of structural changes due to thermal treatments on the gas sensing response is not well studied. All the earlier works on gas sensing of copper ferrite were on the tetragonal phase. In this work, we have chosen sol gel combustion technique for synthesis of the powder samples. Sol gel combustion is a versatile technique (leads to synthesis of nanocrystalline powders and which in turn may cause interesting gas sensing behaviour) and may be scaled to mass production. Recently, there have been many reports on the sol gel combustion technique using different reduction agents and eco friendly approaches [12–14].

In this paper, we study the effect of thermal treatment on the structural, magnetic and chemical sensing properties of copper

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ferrite prepared by the sol gel combustion technique.

## 2. Experimental details

Copper ferrite powder was synthesized by the sol gel combustion technique discussed elsewhere [15]. The obtained powder sample was ball milled using yttria stabilized zirconium balls for 24 hours. The samples were then calcined at temperature ranging from 300 to 800 °C. One part of the powder was cooled slowly in furnace and the other part quenched by introducing it directly from the furnace into liquid nitrogen. The following naming scheme was followed. Sample calcined at 300 °C and cooled in furnace was labelled as CuF300FC where as the quenched one was labelled CuF300QN.

Powder samples were characterised using a Panalytical X-Ray diffractometer in the  $2\theta$  range 15–80° for a scanning time of 2 h. The XRD of all the samples (except CuF600QN) were recorded on a Bruker D4 machine for characterising the sample further, using Rietveld refinement. Rietveld refinement was performed on all the recorded XRD data using Fullprof software. XRD measurements were also performed at different temperatures on a selected sample using D8 Bruker Advance diffractometer equipped with a 1D LynxEye Detector (Cu K $\alpha$ ). XRD spectra were recorded in the temperature range 50–950 °C at intervals of 50 °C. The magnetisation of the samples were measured using a Quantum design physical property measurement system. The  $M$ – $H$  loops were recorded with a maximum applied field of 5 T.

The chemical sensing properties of the samples were analysed using a homemade set up. Resistance was measured using Keithley 181 Nanovoltmeter and Keithley 220 Programmable current source. The resistance measurement unit was connected to desktop PC using Labview software. Sensing measurements were performed using ethanol gas (500 ppm) and zero air (synthetic air with N<sub>2</sub> and O<sub>2</sub>). It was observed that when ethanol was inserted in the chamber, resistance of the ferrite decreased. When the resistance reached a saturation value the ethanol gas was purged with zero air. The response of the sample was defined as the ratio of the change in resistance in the presence of ethanol to the resistance in air.

## 3. Results and discussions

### 3.1. XRD

Fig. 1 shows the room temperature XRD of furnace cooled copper ferrite samples calcined at various temperatures. Sample CuF300FC was compared with JCPDS data card 77-0010 (for cubic copper ferrite).

It was seen that most of the peaks match with cubic copper ferrite. There are some additional peaks, however, which correspond to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (104) and CuO (111) phases. For samples calcined above 300 °C, it can be seen that peaks (in the XRD measured at room temperature) like (220) starts splitting into two (220) and (202) peaks due to the onset of tetragonality. The splitting of the peaks becomes more apparent with increase in calcination temperature, indicating that tetragonal distortion of the sample increases with calcination temperature.

It is observed that the relative intensity of the additional peaks due to the secondary phases present is not the same in all the samples. The relative intensity of the peaks increases with calcination temperature and is highest for CuF600FC sample. In CuF800FC, the peaks corresponding to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> disappears. However a small peak of CuO is still seen at  $\theta$ =38.8°. This peak is not clearly visible in the figure, but can be seen after amplifying the intensity.

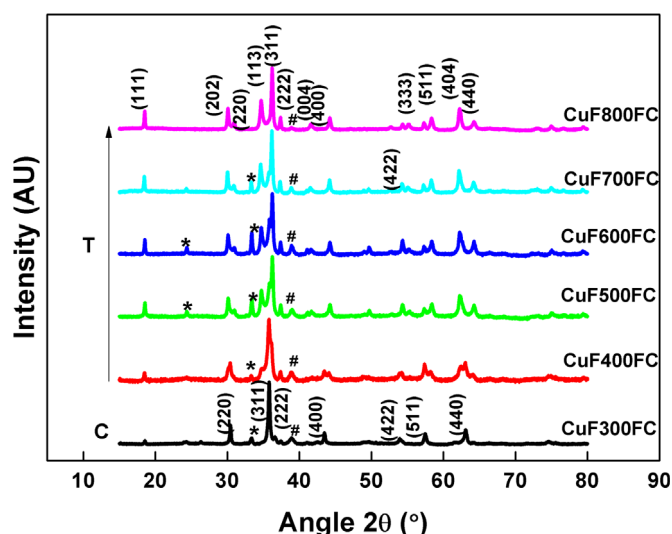


Fig. 1. Room temperature XRD of copper ferrite furnace cooled samples. C and T represent cubic and tetragonal copper ferrite phase respectively. \* represents  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> phase and # represents CuO phase.

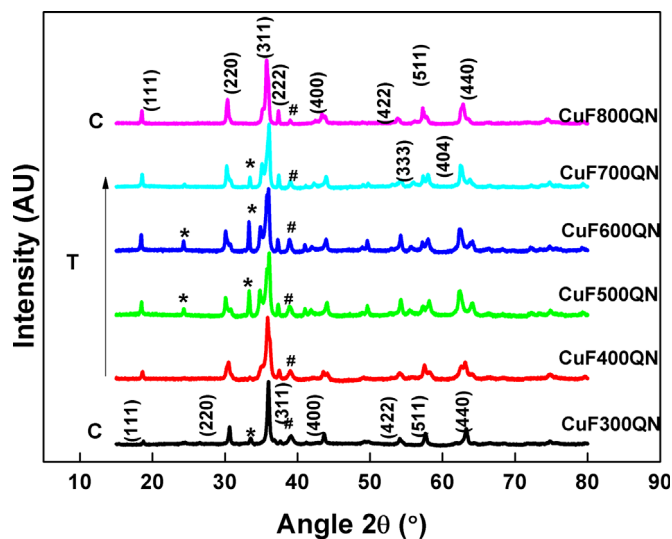


Fig. 2. Room temperature XRD of copper ferrite quenched samples. C and T represent cubic and tetragonal copper ferrite phase respectively. \* represents  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> phase and # represents CuO phase.

Room temperature XRD of quenched copper ferrite samples, calcined at various temperatures is shown in Fig. 2. The main difference from the XRD of furnace cooled sample is that, in case of quenched samples, copper ferrite moves from a cubic phase to tetragonal phase and reverts back to the cubic phase with increase in calcination temperature.

The volume percent of CuFe<sub>2</sub>O<sub>4</sub> present in all samples was calculated from Rietveld refinement and is included in Table 1. From Table 1, it could be seen that the percentage of CuFe<sub>2</sub>O<sub>4</sub> shows an initial increase with calcination temperature at 400 °C and falls at 500 and then again increases above 600 °C. The lower content of CuFe<sub>2</sub>O<sub>4</sub> in samples calcined at 300 °C may be because the temperature is not sufficient for the formation of spinel phase. However, a further decrease in CuFe<sub>2</sub>O<sub>4</sub> content above 400 °C may be due to the precipitation of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and CuO.

There are several reports in the literature on the presence of impurity phases when CuFe<sub>2</sub>O<sub>4</sub> is synthesised in the nanocrystalline powder form [16–19]. The precipitation and disappearance of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> in MgFe<sub>2</sub>O<sub>4</sub> was reported earlier [15]. However there is

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