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# Study of magnesium ferrite nano particles with excess iron content

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ABSTRACT

Stoichiometric and non stoichiometric magnesium ferrite ($MgFe_{2+\delta}O_4$, $\delta=0.0, 0.1$) were synthesized by the sol gel combustion method resulting in nanocrystalline powders with size ranging from 10 to 100 nm. These powders were calcined at various temperatures (300–800 °C). One part of the calcined powder was quenched in liquid nitrogen and the other part furnace cooled. $\alpha$-$Fe_2O_3$ was observed in all calcined samples by XRD and this was also reflected in the magnetization data. Electrical response of $MgFe_{2.1}O_{4+\delta}$ spinel phase to 75 ppm ethanol was found to be greater than that for a stoichiometric magnesium ferrite.

## 1. Introduction

Spinel ferrites are metal oxides with a general formula $MFe_2O_4$. Their magnetic properties have been extensively studied because of their applications [1]. Recently, there have also been studies on the gas sensing behavior of ferrites [2] as the electrical resistance of ferrites can change in response to their gaseous environment. Various ferrites including Magnesium ferrite, Zinc ferrite and Nickel ferrite has been studied for sensing ethanol [2–5]. Other than ferrites, hematite is also useful for ethanol sensing [6]. It is also known that the defects in a system may improve gas sensing performance [7]. Recently the effect of non stoichiometric zinc ferrite with deficient and excess Fe on the ethanol sensing behavior of zinc ferrite was demonstrated [5]. It was shown that excess Fe in spinel helps in improving response towards ethanol.

It is not clearly known, if there is any relationship between the magnetic and gas sensing properties of ferrites. Magnetic properties in magnesium spinel ferrite are largely governed by the site occupancies of ions and are quite sensitive to the thermal treatment given to them [8]. Keeping this in mind and to check if there could be any link between the magnetic properties and the gas sensing properties, we decided to study non stoichiometric magnesium ferrite containing excess iron. In this paper, we report a preliminary study of magnetic and gas sensing properties of magnesium ferrite with 5% excess iron.

## 2. Experimental details

Stoichiometric and non stoichiometric $MgFe_2O_4$ were prepared from Mg $(NO_3)_2 \cdot 6H_2O$ and Fe $(NO_3)_3 \cdot 9H_2O$ by sol gel combustion synthesis. The nitrate salts were taken in molar ratio 2:1 and 2.1:1 for stoichiometric and non stoichiometric samples respectively and were dissolved in distilled water. Citric acid was added to this solution to have 1:1 ratio with metal salts and the resultant solution kept over a hot plate at 80 °C with constant stirring. After the complete dissolution of added salts, ammonia solution (25%) was added until the pH reached 7. The resultant mixture was heated with constant stirring for about 15 h, at the end of which, it transformed to a gel. This gel was further heated without stirring and at an optimum viscosity of the gel, the gel self ignited. The combustion continued till all of the gel had been transformed to a fluffy powder. This powder was then milled in a ball mill with yttria stabilized zirconium balls for 24 h. The resultant powder was then heated in air in the temperature range 300–800 °C. A part of the powder was quenched in liquid nitrogen and the other part was allowed to cool slowly inside a furnace. These powders were then crushed and characterized.

The following scheme was used to name the samples. All the non stoichiometric samples were named with extension '_5'. Furnace cooled samples were indicated as 'FC' and quenched ones as 'QN'. Thus non stoichiometric sample furnace cooled from 800 °C was named as MgF800FC_5% and stoichiometric sample as MgF800FC.

## 3. Characterization

X-ray diffraction experiments were carried out using a Panalytical X-Ray diffractometer with a Cu target ($K_\alpha$ radiation,

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$\lambda = 1.54060$ Å). The powder samples were scanned in the $2\theta$ range 20–80° with a step size 0.02°. Field Emission Gun Transmission Electron Microscopy (FEG-TEM) images were taken using JEOL JEM-2100F microscope. M–H measurements were carried out at 5 K on a Quantum design Physical property Measurement System (PPMS) having a Vibrating Sample magnetometer (VSM) attachment.

Gas sensing measurements were performed using a homemade set up. Two set of samples were prepared for gas sensing. In the first case, powder samples were pressed using a uniaxial pressure of 1.44 MPa. These are termed as green pellets in the present paper. Electrical contacts were made in these pellets using silver paint. In the second case, powder was mixed with 10% binder (poly vinyl alcohol) and then pressed using a uniaxial pressure of 1.44 MPa. The second set of pellets was sintered at 800 °C following a binder burnout cycle at 500 °C for 12 h. These pellets are termed as sintered pellets here. These pellets were metalized using a thin film of silver deposited using DC sputtering. For the gas sensitivity test, 75ppm ethanol and air (0% humidity) were used. The test gases were streamed alternatively into the chamber containing the test sample attached to a heater. Resistance measurements were performed using a Keithely 220 Nanovoltmeter and a Keithley 181 current source connected to computer using Labview software.

## 4. Results and discussions

### 4.1. X-ray diffraction (XRD)

Fig. 1a and b show the XRD pattern of furnace cooled and quenched Fe excess $MgFe_2O_4$ powder samples. The observed peaks were matched with JCPDS card no 73-1720 and 33-0664 for $MgFe_2O_4$ and $\alpha$-$Fe_2O_3$, respectively.

From Fig. 1a and b, it can be seen that the samples have formed the magnesium ferrite phase. In addition to that a phase of $\alpha$-$Fe_2O_3$ is also seen for all samples. It is also seen that the relative intensity of (1 0 4) peak of $\alpha$-$Fe_2O_3$ (highest intensity peak of $\alpha$-$Fe_2O_3$) is not the same in all spectra. The intensity of (1 0 4) peak of $\alpha$-$Fe_2O_3$ initially increases with calcination temperature, with a maximum observed for MgF600FC_5 and MgF500QN_5 and then decreases at higher temperatures. This indicates that some of the excess Fe added to the system is precipitating as $\alpha$-$Fe_2O_3$ phase for all samples. Similar observation has been reported by other workers [9].

Table 1 gives the amount of $\alpha$-$Fe_2O_3$ in all samples obtained from Rietveld refinement. It can be seen from Table 1 that, this amount is not same in all the samples. The amount is greater than 5 mol%, for samples calcined and furnace cooled or quenched from 500 and 600 °C. For sample MgF800FC_5, the amount of $\alpha$-$Fe_2O_3$ phase is only 0.2%.The ability of spinel structure to accommodate excess Fe ions has been already shown and the quantity of excess Fe ions that can be accommodated increases as a function of calcination temperature [10,11].

### 4.2. FEG-TEM

The FEG-TEM images of MgF600FC_5 furnace cooled sample is shown in Fig. 2 along with the selected area diffraction (SAED) pattern in inset. MgF600FC sample was chosen as it is having the largest amount of $\alpha$-$Fe_2O_3$ phase (8.1%) from the Rietveld refinement. It can be seen from Fig. 2 that MgF600FC_5 sample contains cluster of both large particles and small particles. The SAED on smaller particles (shown in the inset), shows that these particles are in $\alpha$-$Fe_2O_3$ phase.

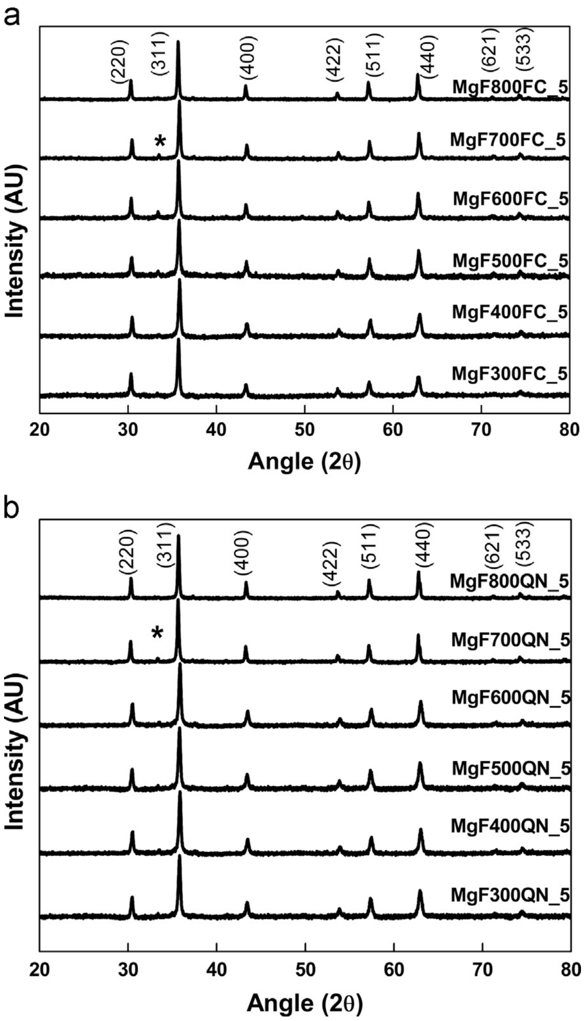

**Fig. 1.** XRD of (a) Furnace cooled and (b) Quenched samples. * represents (1 0 4) peak of $\alpha$-$Fe_2O_3$.

**Table 1**
Mol% of $\alpha$-$Fe_2O_3$ and $\chi^2$ from Rietveld.

| Calcination temperature (°C) | Furnace cooled | | Quenched | |
|---|---|---|---|---|
| | Mol% of $\alpha$-$Fe_2O_3$ | $\chi^2$ | Mol% of $\alpha$-$Fe_2O_3$ | $\chi^2$ |
| 300 | 2.9 | 1.73 | 1.9 | 1.42 |
| 400 | 4.5 | 1.75 | 4.4 | 1.64 |
| 500 | 6 | 1.55 | 7.3 | 1.46 |
| 600 | 8.1 | 1.42 | 5.7 | 1.49 |
| 700 | 4.5 | 1.47 | 5.1 | 1.54 |
| 800 | 0.2 | 1.69 | 2.8 | 1.58 |

### 4.3. Magnetic measurements

Magnetic measurements were performed on all the furnace cooled and quenched samples at 5 K. Due to the non saturation of magnetization in these samples, value of magnetization was calculated using the law of approach to saturation magnetization [12] and the value at H→∞ is being reported. The change in the value of magnetization is plotted as a function of calcination temperature in Fig. 3a and b. It can be seen that the values of magnetization is not increasing monotonically both for furnace cooled and quenched samples. For samples calcined from 500 to 800 °C, the value of magnetization for quenched samples is higher than the corresponding furnace cooled ones. The conversion of

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