Synthesis of Mn$_{1-x}$ Zn$_x$ Fe$_2$O$_4$ ferrite powder by co-precipitation method

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Abstract. Ferrimagnetic substances referred to as ferrites are ionic crystals whose chemical composition is of the form XFe$_2$O$_4$ where X signifies a divalent metal. Magnetic Nano sized ferrites have found a significant potential in many applications, such as magnetic recording media, Ferro fluids and radar absorbing coating. Ferrites are widely used in many industrial applications due to their spontaneous magnetization. Soft ferrites of Mn-Zn, Ni-Zn and Mg-Mn are well known for their high magnetic permeability. In the present research work we have prepared fine Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ ferrite powder with varying x concentrations (0.25-0.75) by metal chloride precursors through a co-precipitation technique by pipette drop method using aqueous NaOH solution for comparing their spontaneous magnetization and particle size. The co-precipitation technique is a high way to produce chemically homogeneous powder with fine particle size in nanometers (22.5nm-74.5nm). The effect of x-concentration on the particle size of the Mn$_{1-x}$ Zn$_x$ ferrite has been discussed on the basis of XRD. The crystalline phases have been identified by X-ray diffraction with Cu-Kα radiations. The XRD patterns have verified that the specimen has spinal type structure. The observable peaks are broad since the size of the particles is small. We have concluded that at constants temperature particle size increases with increasing x-concentrations. Effect of different concentrations of x (Zn$^{+2}$) on the spontaneous magnetization of different Mn$_{1-x}$ Zn$_x$ Fe$_2$O$_4$ samples is determined. We have reached the conclusion that all the samples of Mn$_{1-x}$ Zn$_x$ Fe$_2$O$_4$ ferrites were magnetic either of low or high magnetization. The maximum spontaneous magnetization and minimum particle size is obtained at x=0.25 (at digestion temperature=65°C).

1. Introduction

The study of spinel ferrites in the nanoregime gets significance from a fundamental point of view as well as an applied perspective. Mn-Zn ferrites, among all the ferrites, are commercially the most important class of materials. Soft ferrites such as Mn-Zn, Ni-Zn and Mg-Mn are well known for their high magnetic permeability [1]. Current research efforts have been concentrated on synthesizing nanometre sized (22.5-90 nm) ferrite particles to minimize energy losses associated with bulk systems. Mn and Mn-Zn ferrites both have been proved as essential materials for higher frequency (up to MHz) applications such as inductors and transformers [2].

The structural and magnetic properties of ferrites are found to be sensitive to their composition and microstructure, which depends upon the processing conditions. Chemical co-precipitation was selected as a best method to synthesize nanoparticles. Co-precipitation is the least expensive and the simplest approach for making nanoparticles. This method produces nanoparticles in large quantities (order of grams) in a relatively short interval of time and utilizes inexpensive and readily available chemicals as precursors. Inexpensive iron salts may be mixed with a precipitating agent such as NaOH to form nanoparticles of iron oxides [3]. In Co-precipitation, the nucleation and growth steps overlap, but the particles are usually harvested in the time period before Ostwald ripening fully takes into effect.
X-ray diffraction technique is used to study the effect of variation in the Zn concentration and its effect on particle size and spontaneous magnetization [4]. In the present work Mn-Zn ferrites are prepared by Co-precipitation technique and subsequent digestion process (below 100°C). Digestion, which is an Ostwald ripening process, did not change the crystalline structure but increased the particle size and crystallite size. The particle size is characterized by using XRD [5].

2. Experimental Details
Manganese zinc ferrites belonging to the series of Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ (x = 0.25, 0.50, 0.75) were synthesized by wet chemical co-precipitation technique and digestion process. The samples with varying x concentration were prepared. The value of x was 0.25, 0.50, and 0.75. For each sample the concentration of both NaOH and FeCl$_3$ were kept constant. For each sample the ratio Fe: Na was taken 1:4. All the salts MnCl$_2$ 4H$_2$O, ZnCl$_2$ and FeCl$_3$ with different quantities for different samples were dissolved in distilled and de-ionized water [6].

The beaker containing 100 ml solution of NaOH was placed on magnetic stirrer of moderate speed (50rpm) at room temperature. The solution of beaker containing metallic ions was added drop by drop into the beaker containing NaOH solution. During the addition dark grey precipitates were obtained. The beaker containing the dark grey precipitates was placed into pre-heated water bath containing water and ethylene glycol. The temperature of water bath was varied from sample to sample. Digestion was performed for 85 minutes. The particles were settled down at the bottom of the beaker after 85 minutes. The beaker was cooled to a moderate temperature after taken out from water bath. The particles were obtained through filtration. The filtered particles were dried at 50°C in an oven for 18 hours. Finally the fine materials were yielded and powder form was obtained [7-8]. The spontaneous magnetization of the particles was checked with the help of permanent magnet. These samples were characterized by x-ray powder diffraction technique using Cu K$_\alpha$ radiation ($\lambda = 1.5405$ Å). Lattice parameter of these samples of different compositions was calculated. The average crystallite size of each sample was estimated by employing the Debye–Scherrer formula.

3. Results and Discussion
The properties of ceramics are greatly affected by the characteristics of the powder, such as particle size, morphology, purity and chemical composition. Using chemical methods, e.g. co-precipitation, sol-gel, hydrothermal and colloid emulsion technique, it has been confirmed that they efficiently control morphology and chemical composition of the prepared powder [9]. Among these wet chemical technique, sol-gel using alkoxides, hydrothermal and colloid emulsions are time consuming and involve highly unstable alkoxides and difficult to maintain reaction condition. Co-precipitation is one of the more successful techniques for synthesizing ultrafine powders having narrow particles size distribution [10-11]. This process can avoid complex step such as refluxing of alkoxides, resulting in less time consumption compared to other techniques. [12].

The x-ray diffraction patterns of mixed ferrites belonging to the series Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ is shown in fig. a, Fig. b and Fig. c They are found to be characteristic of a spinel structure [13].
Spontaneous magnetization was checked with the help of permanent magnet. All the samples of Mn\textsubscript{1-x}Zn\textsubscript{x}Fe\textsubscript{2}O\textsubscript{4} showed spontaneous magnetization whether of low or high magnetization.

3.1. Discussion on the results of XRD patterns

3.1.1. Comparison between 0.25g concentration samples

In this study MnZn Fe\textsubscript{2}O\textsubscript{4} was prepared by varying the digestion temperature. Temperature of the water bath was kept at 65\textdegree\textnormal{C}, 75\textdegree\textnormal{C} and 95\textdegree\textnormal{C}. Each sample was hosted in water bath for 85 minutes. According to the calculated particles sizes, the particle size of sample 1 which was 22.35 nm prepared at 65\textdegree\textnormal{C} was found better as compared to others samples (e.g. sample 2 = 36.18nm, sample 3 = 45.29nm) of 0.25g concentrations.

3.1.2. Comparison between 0.50g concentration samples

In this study MnZn Fe\textsubscript{2}O\textsubscript{4} was prepared by varying the digestion temperature. Temperature of the water bath was kept at 65\textdegree\textnormal{C}, 75\textdegree\textnormal{C} and 95\textdegree\textnormal{C}. Each sample was hosted in water bath for 85 minutes. Spinel peak of sample 4 prepared at 65\textdegree\textnormal{C} of digestion temperature was more prominent as compared to sample 5 and sample 6. According to the calculated particles sizes sample 6 = 57.25nm (prepared at 95\textdegree\textnormal{C} digestion temperature) was better as compared to sample 4 and sample 5. The characteristic peak was obtained at an angle of 33, 35.86 and 35.66 degree 2 theta with Cu K\alpha x-rays.

3.1.3. Comparison between 0.75g concentration samples

In this study MnZn Fe\textsubscript{2}O\textsubscript{4} was prepared by varying the digestion temperature. Temperature of the water bath was kept at 65\textdegree\textnormal{C}, 75\textdegree\textnormal{C} and 95\textdegree\textnormal{C}. Each sample was hosted in water bath for 85 minutes. Spinel peak of sample 8 prepared at 75\textdegree\textnormal{C} of digestion temperature was more prominent as compared to sample 7 and sample 9. According to the calculated particles sizes sample 7 = 57.25nm (prepared at 65\textdegree\textnormal{C} digestion temperature) was better as compared to sample 8 and sample 9. The characteristic peak was obtained at an angle of 35.66, 35.228 and 35.36 degree 2 theta with Cu K\alpha x-rays.

3.1.4. Comparison between 0.25g, 0.50g and 0.75g concentration samples

It was observed that variation in concentration from 0.25g to 0.75g changed the size of the particle(as shown in table 1) but peak intensity of the concentration 0.50g(as shown in Fig. 2) showed that it had better magnetic qualities. So concentrations 0.50g had better crystal structure and had spinel-type structure. [8]
3.2. Particle Sizes

Particle sizes of the prepared manganese zinc ferrites were measured with the help of Debye–Scherer formula using the peak of maximum intensity for each pattern [14]. The peak of maximum intensity for each sample was obtained at angle 34.60, 35, 35, 33, 35.86, 35.66, 35.66, 35.228 and 35.36 respectively. The particle size so calculated is given in Table 1.

| Sample No. | X  | Particle Size (nm) |
|------------|----|--------------------|
| 1          | 0.25 | 22.35              |
| 2          | 0.25 | 36.18              |
| 3          | 0.25 | 45.29              |
| 4          | 0.50 | 72.94              |
| 5          | 0.50 | 74.51              |
| 6          | 0.50 | 57.25              |
| 7          | 0.75 | 57.25              |
| 8          | 0.75 | 74.51              |
| 9          | 0.75 | 90.58              |

Table 1. Particle sizes of the sample

The particles sizes calculated for all the nine samples at different digestion temperatures and with varying Zn concentrations (x) 0.25, 0.50 and 0.75 are 22.35, 36.18, 45.29, 72.94, 74.51, 57.25, 57.25, 90.58 and 74.51 (nm) respectively, using Debye–Scherer formula. This showed that the particle size of MnZn ferrites increased with increase in the concentration of (x). The minimum particle size obtained was 22.35 nm which is comparable to particle size obtained in the previous work of Dunlap et al. (2003).

4. Conclusions

At constant temperature, particle size increases with increasing x concentration. The maximum spontaneous magnetization and minimum particle size was obtained at x = 0.25 at digestion temperature 65°C.
5. References

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