MICROWAVE ASSISTED SYNTHESIS OF FINE MAGNETIC MANGANESE FERRITE PARTICLES USING CO-PRECIPITATION TECHNIQUE

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Co-precipitation technique results in the better homogeneity of the particles as compared to the conventional ceramic technique. However, there is a range of concentration ratios of the reacting compounds which result in the particles of required properties. In this work, the co-precipitation technique has been utilized to synthesize homogeneous ferrite nano particles. The manganese ferrite has been synthesized using $MnCl_2.4H_2O$, $FeCl_3.6H_2O$ and NaOH. The standard co-precipitation route was used to synthesis fine particles. First we dissolved the metallic salts of Manganese and iron in distilled and de ionized water, the metal ion solution was then reacted with the NaOH solution. The resulting precipitate was brought to temperatures of 60^{o}C to 100^{o}C for digestion times of 20 minutes and 60 minutes. The subsequent digestion process was performed to obtain equilibrium particle size. Different effects were studied such as effect of concentrations, effect of duration on digestion and digestion temperature on the structural properties of the particles. It was studied that for the formation of Mn ferrite an increase of pH value up to 12.5 accelerated the formation of the ferrite. But a further increase of pH up to 14 led to a reduction of the ferrite yield. The solutions were then oven dried or treated with microwaves. The effect of conventional thermal treatment and of the microwave treatment was compared and it was found that the microwave treatment results in greater spontaneous magnetization. The powder x ray diffraction technique was used to examine the ferrite phase of the particles. The particle size was calculated by Scherer's formula using the broadening of the characteristic (311) peak of the spinel ferrite in the range of 18.7-23.9 nm.
Keywords: Co-precipitation, magnetic particles, manganese ferrite, nanometer, microwave, particle size

INTRODUCTION

Magnetic materials have been playing a key role in the data storage on audio and video-tape (Chalyi, 1970 and Omar, 1974) as well as on computer disks. They are also used in the body scanners as well as a wide range of applications. The entertainment and recording market relies on magnetic materials in applications such as PCs, CD players, televisions, game consoles and loud speakers. (Hsu *et al.* 1991).

In fundamental sciences the Spinel Ferrite magnetic nanoparticles are of great interest. In recent times the magnetic properties have been the subject of special interest because of the information they yield about the interactions among the constituents of matter. This information, being truly interdisciplinary, is of interest to physicists, as well as to other scientists and engineers. Magnetic materials have wide-ranging technical applications, which include the transformer cores in electrical machinery, the magnetic tapes in computers. Ferrites offer some distinct advantages that make their future appear promising. Special attention has been paid to the characteristics of powdered ferrite materials to investigate the phase formation (Tang *et al.* 1991).

There have been various synthetic technique involved in the synthesis of ferrites. The co-precipitation technique results in better homogeneity of particles as compared to the conventional ceramic technique. Several studies have been conducted recently to investigate the effect of variation in the synthesis route on the particle size of the ferrites (Auzans *et al*. 1999). For the formation of Mn ferrite an increase of pH value up to 12.5 accelerates the formation of the ferrite (Morelli, 2000). . A further increase of pH up to 14 lead to a reduction of the ferrite yield due to formation of nonmagnetic Na_2 [Mn $(OH)_4$] and paramagnetic hydro-hausmanite $Mn_3O_4.nH_2O$ at high pH (Solis *et al* 2007).

There have been many reports on the structure of manganese ferrite, $MnFe_2O_4$, prepared by co-precipitation from Fe^{+3} and Mn^{+2} and Gillot and Guendouzi, 1986). Manganese ferrite nanoparticles obtained by the chemical co-precipitation and the ferritation are formed in two sequential processes: the proper co-precipitation of metal salts in the presence of an alkaline medium, which occurs immediately, and the transformation of hydroxides into ferrite. The latter process starts at the moment the co-precipitation starts but it requires a certain time and mostly occurs when the precipitate phase is heated. Recently, the ferrites have demonstrated to be good materials for gas sensing applications and Veverka *et al.* 2007).

In the present work we have investigated the effect of several parameters on the particle size distribution of the ferrites. These parameters include the influence of temperature, pH, concentration of reagents, digestion time, thermal treatments using conventional oven and the effect of microwave treatment.

MATERIALS AND METHODS

We have synthesized fine manganese ferrite particles using co-precipitation technique. The salts of $FeCl_3.6H_2O$ and $MnCl_2.4H_2O$ were dissolved in distilled and de-ionized water. In another beaker, solution of NaOH was prepared; the molarity of NaOH solution was ranged from 1 to 2 mol. The two solutions were mixed together on magnetic stirrer with continuous stirring at a moderate speed. The total molarity of the metallic ions calculated for the final volume (after addition of NaOH solution) ranged from 0.05 to 0.25 mol. (Tang *et al.* 1991). After this addition a dark precipitate was obtained. The precipitate was brought into a preheated bath containing water and ethylene glycol for digestion. Digestion was performed at different temperatures. For each sample the temperature was varied from 60˚C to 100^{o}C in steps of 10^{o}C. The time duration for thermal treatment of each sample was kept at 20 minutes and 60 minutes (Bujoreanu *et al.* 2000). The samples were centrifuged to isolate the particles from the solution.

One part of each samples of 60°C to 100^{o}C (digestion temperature) was placed in an oven at a temperature for about 12 hours while the second part of the sample was placed in microwave oven for 3 minutes.

Microwave enhancement can take several forms. Reaction rates can be accelerated, yields can be improved, and reaction pathways can be selectively activated. Fundamentally, microwaves heat things differently than conventional means. This method can reduce the synthesis time. The adoption of the microwave method offers chances to generate new material structures that cannot be obtained from conventional methods (Kamazawa *et al.* 1999). X-ray powder diffraction analysis was performed after each thermal treatment with a Rigaku Rint 2000 series diffractometer using Cu$K\alpha$ radiation λ=1.54056Å (Leyva et al. 2004).

RESULTS AND DISCUSSION

The X-rays powder diffraction patterns of the samples were used to determine the spinel structure by comparing with the ASTM (American Society of Testing and Materials) data. The broadening of the characteristic peak (311) was used to determine the particle size of the ferrite particles. The mean diameter't' of particles is determined by using the Scherer formula given in equation 1.

$$\mathbf{t = K\lambda / (\beta \cos \theta)} \qquad (1)$$

where **t** is the mean crystal size, **λ** is the x-ray wavelength, **θ** is the Bragg angle**, β** is the excess line broading (radian)**,** B is the line width (radian) and b is broadening (radian), K is the constant which is approximately equal to unity and is related both to the crystalline shape and to the way in which β is defined (Klung and Alexander, 1967). The lattice parameter and particle size were obtained by XRD. The lattice parameters were calculated from the XRD peaks at (220), (311), (400), (422), (511) and (440) (Kim et al. 2001). Comparison of experimental 'd' values with ASTM tables confirmed the formation of manganese ferrite (Auzans et al. 1999).

It was found that the temperatures of 60˚C and 70˚C were not sufficient for the digestion of the precipitates (Zhang et al., 2007). The time intervals of 20 minutes and 60 minutes for digestion at the temperatures of 80˚C, 90˚C and 100˚C revealed the spinel structure. Figure 1 shows the x-ray powder diffraction pattern for manganese ferrite fine particles synthesized at 90^{o}C for 60 minutes. For higher temperatures, i.e. greater than 80^{o}C, the effect of time duration had a very little effect. Figure 2 shows the XRD pattern of the sample prepared at 90^{o}C for 20 minutes. The height of (311) peak is lower, thereby showing the lower level of crystallinity, but the difference is not much significant. The phase structure, crystal size and lattice constants were determined by XRD.

The samples prepared at 60˚C and 70˚C, did not exhibit the magnetic behavior before heating, when these samples were treated with microwave, samples exhibited magnetism.

Effect of Microwave treatment

In order to confirm the effects of thermal microwave heating and oven heating, XRD patterns of sample (80˚C for the duration of digestion time of 60 minutes). Both samples showed spontaneous magnetization. The characteristic peak was obtained at an angle of 35 degree 2Θ with Cu $K\alpha$ radiation.

From XRD patterns of the samples, it came to know that the characteristic peak (311) was dominating in the microwave treated sample as compared to the oven treated sample. Microwave radiation intensities yield enhancement and characterization of the structure features. Microwave treatment has increased the height of the peak (311) significantly. and width of the spinel peak (Zhenyu *et al*, 2007).

Oven treatment also results in a good influence on the magnetic materials. It is a conventional method that is also used for drying the samples. In the XRD patterns of oven treated samples the spinel peak (311) was prominent (Janis *et al*, 2007). In conventional method the colloidal particles interact with each other forming the ferrite particles whereas remaining part is precipitated.

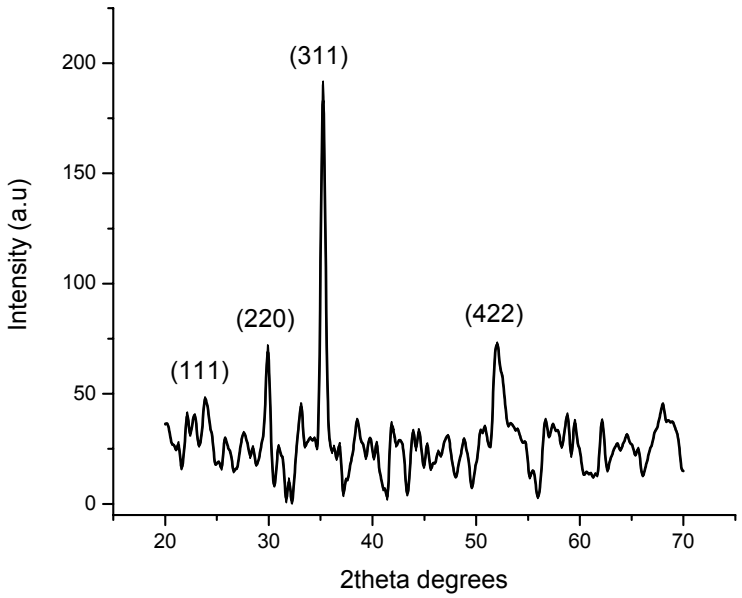

Figure 1. XRD pattern showing the manganese ferrite peaks. The sample was synthesized at 90°C for 60 minutes. The width of the (311) peak was used to determine the particle size of the sample

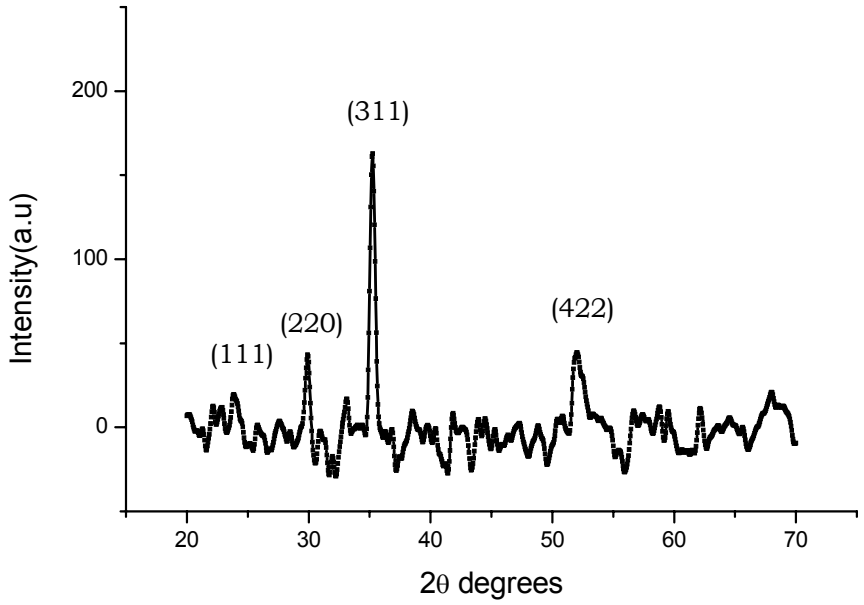

Figure 2. XRD pattern showing the manganese ferrite peaks. The sample was synthesized at 90°C for 20 minutes. The height of the (311) peak is lower than the sample digested for 60 minutes

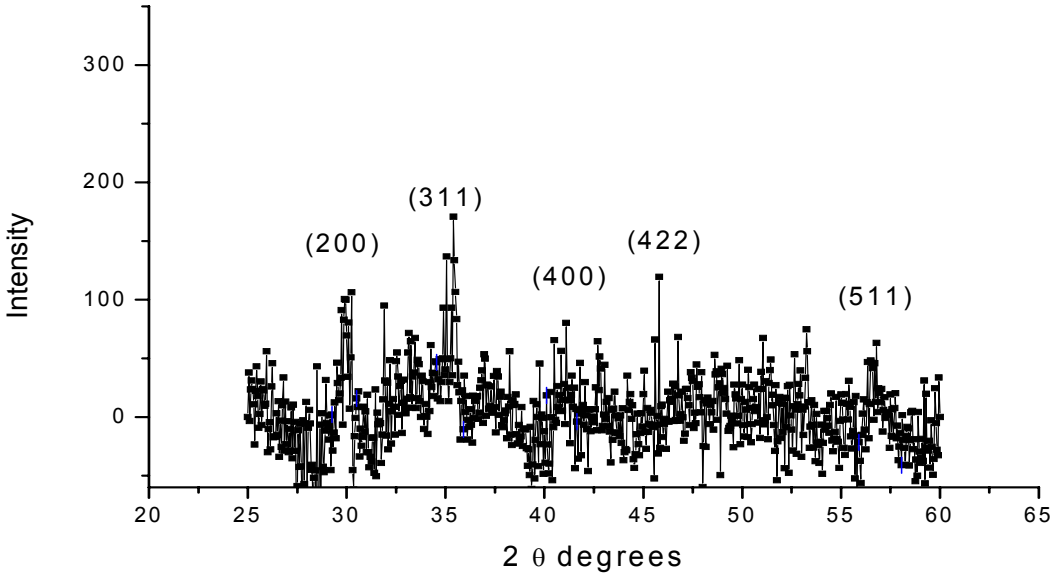

Figure 3. The XRD pattern of sample synthesized at 60°C without microwave treatment. There is no crystalline structure. The locations of the peaks are marked, but there are no significant peaks

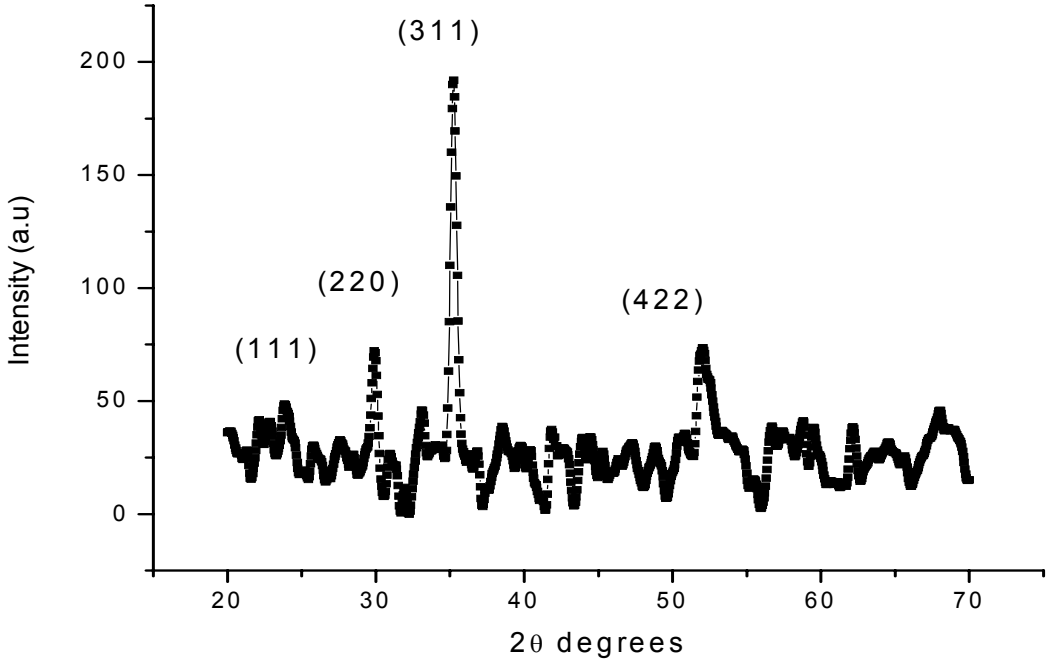

Figure 4. The XRD pattern of the sample synthesized at 60°C with microwave treatment. The effect of treatment is significant. The structure is crystalline and the characteristic peaks are well

Particle size of an oven treated sample was 47.8 nm while that of microwave treated was found to be 23.91 nm. The microwave treatment reduces the particle size and increases the homogeneity of the materials. This is due to the enhanced surface enrichment due to thermal agitation of liquid molecules in microwave field. The apparent change in the material yields improvement which results in the evolvement of new material phases. Microwave treatment is thus a rapid approach that has the capability to control the particle shape and particle size (Shi and Hwang, 2003). It was concluded that microwave treatment improved the spinel crystalline structure of the ferrites.

Effect of concentration

It came to know that the particle size of concentration of 0.1 was found 18.24nm and the particle size of concentration of 0.2 was found 21.15 nm. The height of spinel peak of concentration 0.1 was lesser as compared to the sample of concentration 0.2. (Tang et al., 1991)

So it was concluded from the data that variation in concentration from 0.1 to 0.2 changed the size of the particle but peak intensity of the concentration 0.2 showed that it had better magnetic qualities as compared to the concentration 0.1. So concentration 0.2 had better crystal structure.

Effect of temperature

During this study, a range of temperature from 60˚C to 100˚C was used to digest the precipitate. Comparison of initial results of the materials with the XRD results showed that digestion temperatures near to the 100˚C, exhibited well quality of magnetism.

CONCLUSIONS

It has been concluded that below 80˚C, the particles are in irregular shape and clustered (Kim et al 2001). On treating such particles with microwave, particles exhibited as good magnets. It indicates that microwave has improved the crystallinity of the particles.

Microwave treated particles are spherical, well dispersed and without appreciable clustering. The particle size is almost uniform. By contrasting the Oven and Microwave treatments, it was concluded that both treatments in the co-precipitation technique produced good effects on the materials.

Microwave treated particles have significant spinel peak heights as compared to the oven treated particles from XRD patterns. It indicates that particles after the microwave treatment have better crystallinity than oven treated particles.

The XRD patterns also indicate that the microwave treated particles are homogeneous.

Obtained particles of digestion temperature at 70˚C were non-magnetic initially. Conventional oven treatment did not effect in non-magnetic character. When it was treated in microwave, it exhibited magnetism.

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