A new chemical route for the preparation of fine ferrite powders

P PRAMANIK and AMITA PATHAK

Department of Chemistry, Indian Institute of Technology, Kharagpur 721 302, India

Abstract. Precursors to MFe_2O_4 [spinels ferrites; where M = Ni(II), Co(II) and Zn(II)] have been prepared by the evaporation of polyvinyl alcohol added mixed metal nitrate solution, in presence and absence of urea. The precursor materials have low ignition temperature and are spontaneously combustible at low temperatures (250°C to 400°C). The heat liberated through the process is sufficient for the crystallization of the desired ferrite phase. The urea added process resulted in finer, superparamagnetic particles (12–17 nm) compared to the process without urea (particle size 25–30 nm). The ultrafine ferrite powders obtained have been characterized by X-ray powder diffraction (XRD), thermal gravimetry (TG), differential scanning calorimetry (DSC), infrared spectroscopy (IR), transmission electron microscopy (TEM) and room temperature magnetic measurement studies.

Keywords. Ferrites; chemical synthesis route; polyvinyl alcohol; urea; evaporation; fine particle; Powders.

1. Introduction

Technologically, fine-particle ferrites have been of interest due to their application in the preparation of high density ferrites at low temperatures, pigments and as catalysts (Leech and Campbell 1975). The surface properties and the microstructures of such powders, which control most parameters required for any particular application, often depend on the method of their preparation (Das 1981).

The conventional ceramic method for the preparation of ferrites, though successful for large scale production of bulk powders because of its low cost and easy adaptability, have several limitations (Johnson and Ghate 1985) in the production of fine powders. Long heating schedules and high temperatures, the requisites for the ceramic route, sinter the final product and result in the loss of the fine particle nature of the powders. The method is thus affected by a poor control of particle size, morphology and microscopic homogeneity.

The chemical synthesis routes for the production of fine ferrite powders have overcome many of the limitations of the ceramic method. The important chemical synthesis routes, which have gained substantial popularity over the years, include the precursor compound method (Patron *et al* 1987), the coprecipitation method (Schuele 1959; Pathak and Pramanik 1993), the sol-gel method (Marcilly *et al* 1970; Dishlich 1971), the solvent evaporation method (De Lau 1970; Anderton and Sale 1979), the hydrothermal method (Pannaparayil and Komarneni 1989) and the combustion method (Ravindranathan and Patil 1987). These methods are reported (Das 1983) to result in ferrite particles ranging from 10 to 100 nm.

Although several chemical routes exist for the preparation of fine ferrite powders, the considerations of affordability and versatility of a route still remain as a major challenge for the material scientists involved in the development of new synthetic routes.

In the present investigation, an attempt has been made to establish a new chemical route, which is both affordable and versatile, for the synthesis of fine mixed-oxide powders. In this paper, we report the preparation and characterization of only a class of the mixed-oxide powders, viz. the ferrites. The route involves rapid evaporation or spray drying of a polyvinyl alcohol (PVA) added mixed metal nitrate solution in the presence and absence of urea, followed by the pyrolysis of the evaporated or dried mass. The pyrolysis results in X-ray amorphous or, crystalline ferrite powders.

2. Experimental

2.1 *Preparation of the precursor materials*

To prepare the mentioned oxide systems appropriate amounts of the desired metal nitrates are taken into aqueous solution. 10% (w/v) aqueous solution of PVA (mol. wt. = 1,25,000) is then added to each of the mixed metal nitrate solutions so as to maintain a metal ion : vinyl alcohol monomer unit mole ratio of 1 : 2·5. In case of the urea added process, the urea (by weight) is introduced into the system, with thorough stirring, maintaining the urea to cation mole ratio at unity. The PVA helps the homogeneous distribution of the metal ions in its polymeric network structure and inhibits their segregation/precipitation from the solution. The resulting viscous liquid mixture of PVA metal nitrates is evaporated to dryness or spray dried between 130°C and 150°C to obtain a voluminous organic based fluffy precursor powder.

2.2 *Formation of ultrafine ferrite powders*

Ultrafine ferrite powders are obtained from the thermal decomposition of the carbonaceous precursor material. The heat liberated during the exothermic decomposition of the precursor powder facilitates the solid phase reaction between the constituent metal ions and results in the ferrite phase formation. The exothermic decomposition of the precursor material is accompanied by the evolution of various gases (CO, CO_2, H_2O). The evolution of gases not only helps the products to disintegrate but also helps to dissipate the heat of combustion, thus inhibiting sintering of the fine particles.

To study the influence of calcination temperature and time on the particle size, the precursor powders are calcined at varying heat treatment temperatures (between 400°C to 900°C) for varying periods of time (2 h to 24 h).

2.3 *Physical measurements*

Thermal gravimetric and differential calorimetric (TG/DSC) studies of the precursor material, produced by the PVA evaporation route in the presence and absence of urea, are done on the STA-625 thermal DSC. All experiments are performed in air atmosphere with a heating rate of 10°C/min. The infrared (IR) spectra for the precursor and the heat treated powders are recorded on the Perkin Elmer 883

infrared spectrophotometer from 400 to 4000 cm^{-1} by the KBr pellent method. The X-ray powder diffraction (XRD) patterns for the precursor and the heat treated powders are recorded using Phillips P.W. 1710 X-ray diffractometer with CuK$_\alpha$ radiation and Nickel filter. Transmission electron microscopy (TEM) studies of the prepared powders are done on CM-12 Phillips electron microscope. A vibrating sample magnetometer is used for the room temperature magnetic studies of the prepared powders.

3. Results and discussion

The simultaneously recorded TG and DSC data for the NiFe$_2$O$_4$, CoFe$_2$O$_4$ and ZnFe$_2$O$_4$ precursor powders produced by PVA added mixed metal nitrate solution evaporation method, in the presence and absence of urea, follow a similar trend. The thermograms reveal that the precursor powders, produced in the presence and absence of urea, both involve a single step decomposition between 200°C to 400°C. The precursor powders, in the absence of urea, are found to decompose between 210°C to 360°C with an exothermic peak at 302°C. The process involves an exothermic heat liberation of 280·24 mcal/mg with 16·64% weight loss. The exothermic heat liberation is due to the combustion of the carbonaceous remains of PVA and the decarboxylation of the precursor material, which is accompanied by the evolution of gases such as CO, CO$_2$ and H$_2$O (water vapour). The thermal effects are thus accompanied by weight loss in TG curve. While the precursors, in the presence of urea, are found to decompose over a wider temperature region (between 190°C and 410°C) with an exothermic peak at 341·5°C. The heat liberated in the process is also higher (398·5 mcal/mg) and so is the weight loss (18·64%). This is because, here the combustion of the carbonaceous remains of PVA is additionally accompanied by the decomposition of the organic residue from urea, which begins to decompose around 200°C. Hence, the exothermic heat generated is more, which is accompanied by larger amounts of gas evolution. This is manifested by higher weight loss in the TG curve.

IR spectra for all the precursor powders, prepared in the presence or absence of urea, are similar. The IR band at 3387 cm^{-1} and bending mode at 1619 cm^{-1} in the precursor material, could be due to the presence of moisture in the precursor material. The intensity of these bands diminishes and vanishes with the increase in heat treatment temperature. The absorption bands at 1394 cm^{-1} (strong), 1087 cm^{-1} (strong), and at 822 cm^{-1} (weak) in the precursor material, can be assigned to the various vibrational modes of the carboxylate ions. Since, during the complete evaporation process of the starting solution, the metal nitrates get decomposed in presence of the carbonaceous remains of the PVA and correspondingly carboxylate salts and oxides are expected to form. This absorption band disappears after heat treatment at 450°C. The absorption at 578 cm^{-1} and 420 cm^{-1} are due to the lattice absorption of NiFe$_2$O$_4$ (Grimes and Collect 1971). These bands increase in intensity with high heat treatment temperatures of the precursor powder.

The XRD of the powders, produced from the PVA evaporation route in presence of urea (figure 1), reveals that the precursor powders are X-ray amorphous. It also shows broad peaks of the corresponding ferrite phase for the precursor powders calcined at 450°C for the varying periods of time. This indicates the growth of
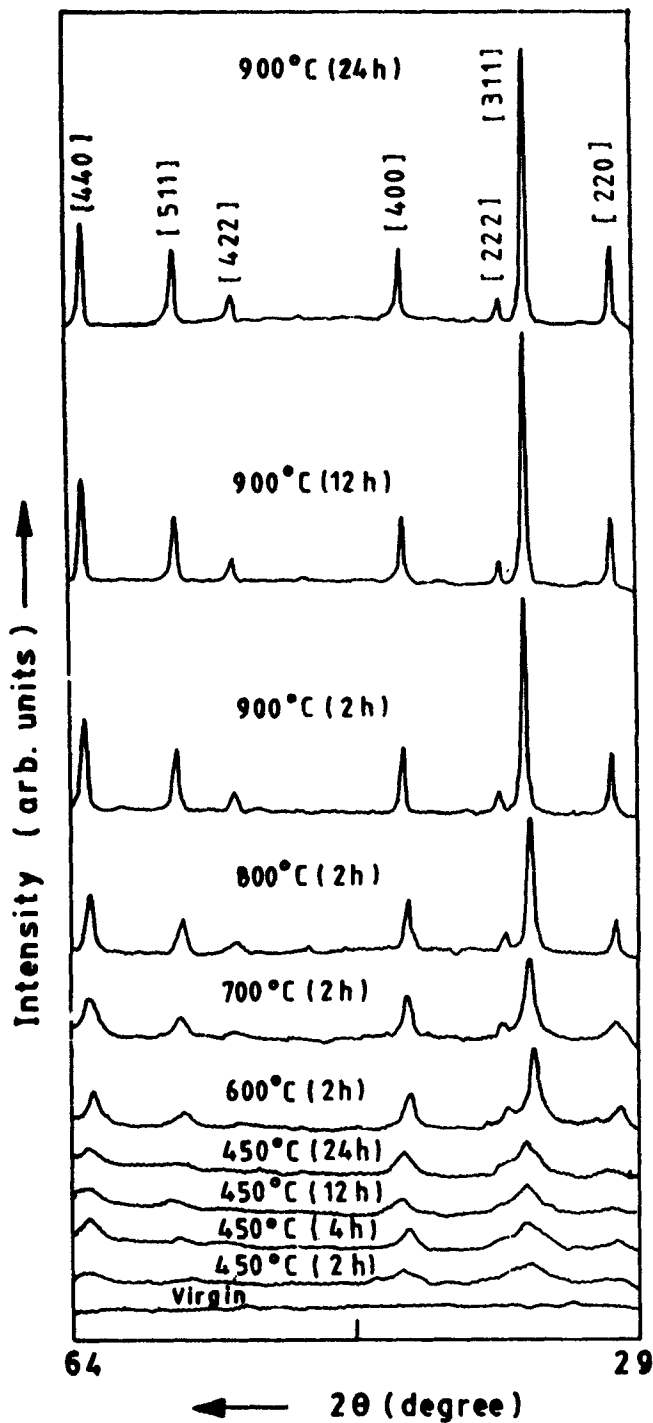
Figure 1. X-ray diffractograms of $NiFe_2O_4$ precursor powders, prepared in the presence of urea, with varying calcination temperatures and time.
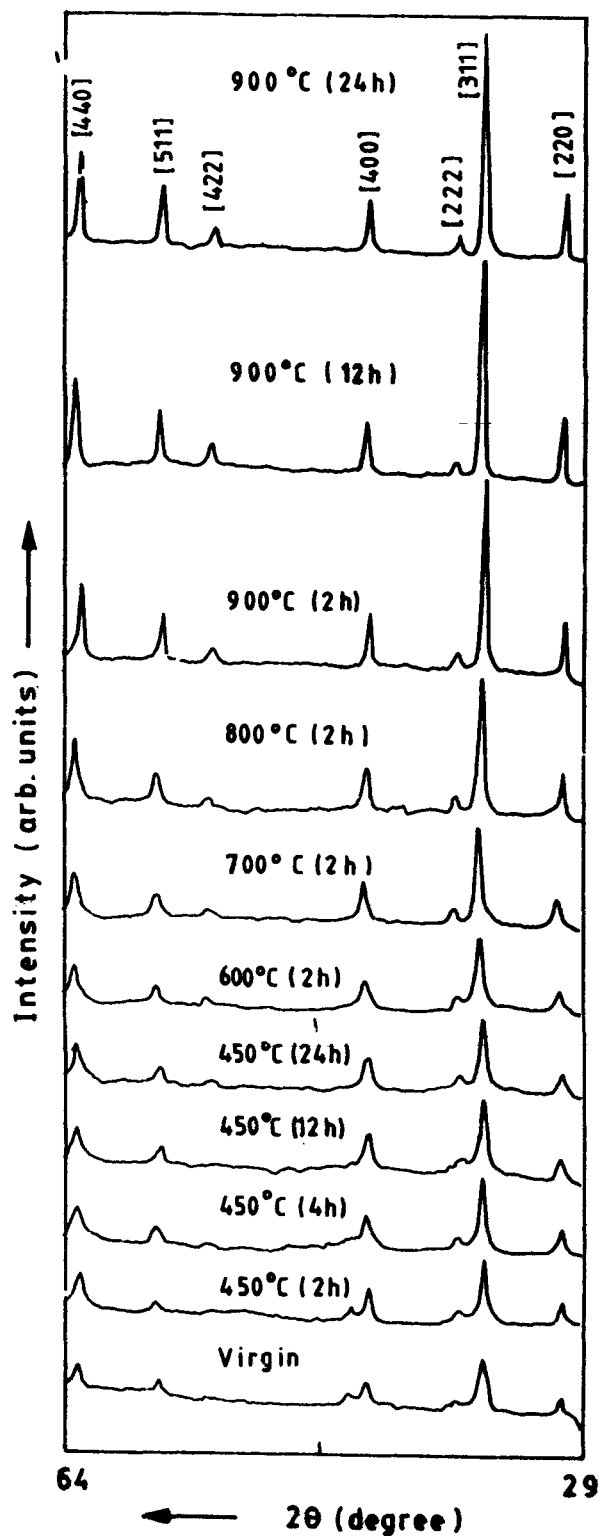
Figure 2. X-ray diffractograms of NiFe$_2$O$_4$ precursor powders, prepared in the absence of urea, with varying calcination temperatures and time.

crystallinity in the precursor powders after thermal decomposition at 450°C and with subsequent heat treatments. While XRD of the precursor powders, prepared in the absence of urea in the PVA evaporation route (figure 2), shows the formation of the corresponding ferrite phase before calcination. The XRD peaks, corresponding to the ferrite phase, increase in intensity with subsequent heat treatments. This indicates the growth of crystallity in the powders with increase in heat treatment temperature and time.

The crystallite size of the prepared powders are determined from XRD line broadening using the Scherrers' equation (Klung and Alexander 1974). These studies reveal that with the increase in the calcination temperature the crystallite size gradually increases for all the powders. The crystallite size variation with calcination period, though has a linear increasing trend, is not very pronounced. It also shows that at low heat treatment temperatures (< 700°C), the powders prepared by PVA evaporation route in presence of urea, yield finer crystallites (~ 170 Å) compared to the crystallites (~ 245 Å) of the powder prepared in absence of urea. In addition, it is also found that on high temperature heat treatment, the powders prepared in both the presence and absence of urea, attain similar values of crystallite size (~ 350 Å). TEM studies support XRD line broadening results. TEM micrographs show that the low temperature (< 700°C) heat treated powders, prepared in presence of urea, result in finer particles compared to the powders prepared in the absence of urea. The average particle size (as observed from TEM) of powders, prepared in the presence of urea, after heat treatment at 400°C, is found to be between 12 17 nm (figure 3a). These powders show polycrystalline ring diffraction pattern in TEM (figure 3b), corresponding to the spinel structure indicating the fine particle nature of the powder. While, the average particle size of the powders, prepared in absence of urea and heat treated at 450°C, is found to lie between 25 to 30 nm (figure 4). These powders show single crystal diffraction pattern in TEM, corresponding to the respective spinel structure. High temperature (>800°C) heat treatment of the same powders, prepared either in the presence or in the absence of urea, results in similar values of particle size (100 nm to 120 nm), as depicted in the TEM micrographs.

The room temperature magnetic studies reveal that the $NiFe_2O_4$ and $CoFe_2O_4$ powders, prepared in the presence of urea and heat treated at 450°C for 4 h, show superparamagnetic behaviour. While the powders prepared in the absence of urea are not superparamagnetic. Superparamagnetism is inferred by zero hysteresis in the B-H curve. The superparamagnetism observed in the powders vanishes when the same is heat treated beyond 500°C.

3.1 *The role of polyvinyl alcohol*

In the PVA added metal nitrate solution evaporation, the PVA plays a dual role.
   (i) When the optimum amount of PVA is added to the mixed metal nitrate solution, the polar groups of the long chain of the polymer play a wrapping and covering role for the cations in the solution. As a result their mutual contact is avoided and so the cations do not grow in size. Thus the metal ions remain uniformly distributed in the viscous liquid during evaporation and their segregation and precipitation from the solution are avoided.
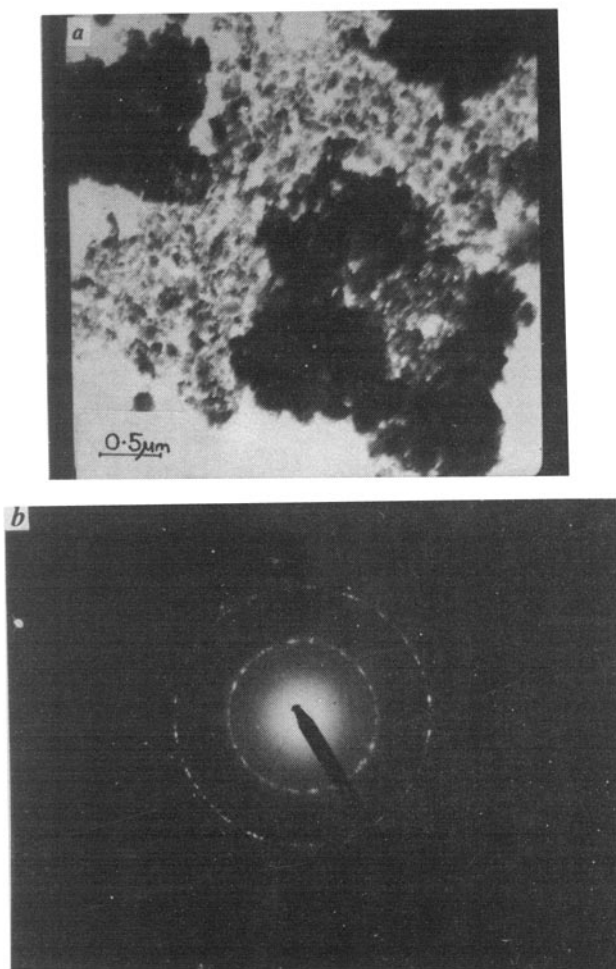
Figure 3. a. TEM micrographs of $NiFe_2O_4$ precursor powders, prepared in the presence of urea, after calcination at 450°C for 4 h and **b.** TEM diffraction of $NiFe_2O_4$ precursor powders, prepared in the presence of urea, after calcination at 450°C for 4 h.

(ii) The carbonaceous material, obtained from the complete evaporation of PVA, provide heat through combustion for the formation of fine single phase ferrite powders at a relatively low external temperature.

3.2 *Role of urea*

The addition of urea to PVA added metal nitrate solution, when evaporated to a pasty mass, acts as a retardant. It stops the crystallization of the precursor powder during complete evaporation of the PVA added solution. Moreover, the DSC studies reveal that the precursor powders, prepared in presence of urea, decompose over a wider temperature range compared to the precursor powders prepared in absence
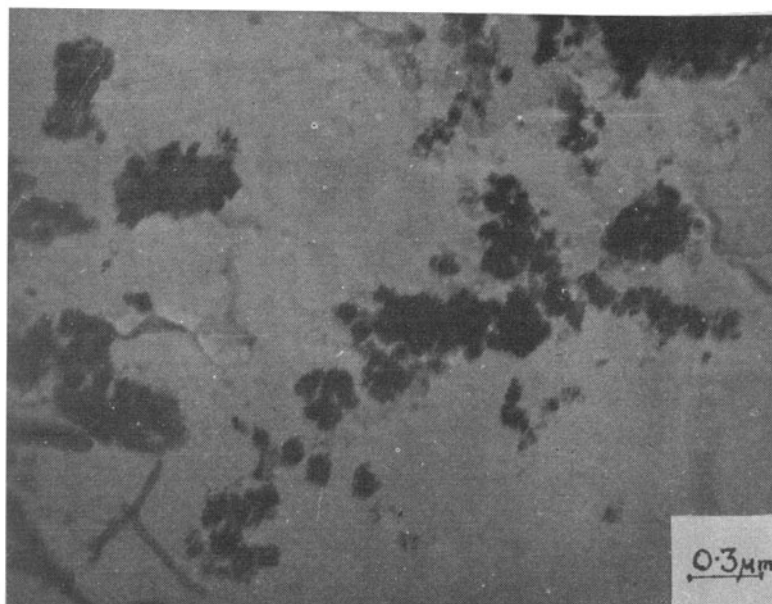
Figure 4. TEM micrographs of $NiFe_2O_4$ precursor powders, prepared in the absence of urea, after calcination at 450°C for 4 h.

of it. This homogenizes the bed temperature and local sintering of the powder is avoided and formation of fine particles occur.

4. Conclusion

The PVA added metal nitrate solution evaporation method, in presence/absence of urea, is technically simpler, cost effective, and more time- and energy-efficient than the other reported chemical method for the preparation of fine single phase mixed-oxide powders. The route can be applied for the preparation of a variety of mixed-oxide systems at relatively low external temperatures.

Another major advantage of the route is that the PVA easily decomposes exothermally at 500°C, leaving behind very little carbon residue.

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