

INFLUENCE OF METAL NITRATE TO FUEL RATIO ON THE MAGNETIC PROPERTIES OF NiFe_2O_4

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ABSTRACT

Objective: Nickel ferrite nanoparticles with dimensions below 30 nm have been synthesized by sol-gel auto-combustion process. The nitrate-citrate gels were prepared from metal nitrates and citric acid solutions under various molar ratios of the metal nitrate to citric acid of 1, 2, 3, 4 and 5 by sol-gel process. The results showed that nitrate citrate gels exhibit a self propagating behaviour after ignition in air at room temperature. The ratio of nitrates to citric acid also affects the combustion process. The as-prepared powder was annealed at 500°C for 6 hrs. The phase composition and structural properties of the obtained samples are investigated by X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). Analysis of the XRD patterns showed the presence of $\alpha\text{-Fe}_2\text{O}_3$ phase and other reflections corresponding to cubic spinel structure. The lattice constant obtained from XRD data increases with metal nitrate to fuel (citric acid) ratio. PACS No: 75.50.Gg, 74.25.Ld, 43.35.Cg

Keywords: - Nickel ferrite, Sol-gel auto combustion, nitrate-citric fuel ratio.

INTRODUCTION

Ferrites have wide range of technological applications depending upon their properties such as saturation magnetization, Curie temperature, density, grain size etc. [1]. The properties of ferrites are known to be sensitive to the processing technique [2] as well as processing parameters. Synthesis of advanced ceramics of nanoparticles is currently gaining wide spread interesting materials. They exhibit superior electrical, dielectric and magnetic properties as compared to their bulk materials [3, 4]. They have been extensively investigated by many researchers because of their importance in many technological applications [5-7]

Ferro-spinel (MFe_2O_4 , where M is Fe, Co, Ni, Mg) are a very important group of magnetic materials covering wide range of applications. There is growing interest in nanoparticles of magnetic ferrites because of their wide applications in electronic devices, magnetic drug delivery, ferro-fluids, permanent magnets, information storage, micro-wave devices etc. [8].

It is well known that the magnetic behaviour of ferrites is largely governed by $\text{Fe}^{3+}\text{-Fe}^{3+}$ interaction [9]. The distribution of cations depends on the method of preparation and preparation conditions. In recent years, processing of ferrites by non conventional solution techniques has gained importance with a view to obtain high quality and high performance materials for various applications. Magnetic properties of ferrite are also directly related to the distribution of the cations over tetrahedral A and Octahedral B sites. Bulk nickel ferrite is presumed to be display an inverse spinel structure [10]. In the case of nanoparticles the structure can deviate from the bulk [11, 12]. This implies that synthesis methods and synthesis parameters has a marked impact on the cation distributions and hence the magnetic properties.

Recent interest in the study of several spinel type ferrites is in terms of the synthesis of their nanoparticles at low temperature by different techniques such as sol-gel [13], co-precipitation [14], hydrothermal [15], citrate precursor [16], ball-milling [17] etc. Among the spinel ferrites, nickel ferrite is a soft magnetic material having low magnetic coercivity and high resistivity values. Nickel ferrite is one of the most important magnetic materials extensively used in high frequency applications due to its high electrical resistivity and low eddy and dielectric losses. Sol-gel and co-precipitation methods may consider as some of the most important

non-conventional methods for the preparation of nano particles. The high reactivity of powders prepared by sol-gel process arises from the better chemical homogeneity of the low precursor mixtures. The sol-gel method is a useful and attractive technique for the preparation of nano sized particles because of its advantages; the good stoichiometry controlled and production of ultra fine particles with nano size distribution in a relatively short processing time at low temperatures.

A small variation in the processing parameters of the ferrite affects its properties greatly. However, the effect of various synthesis parameters like sintering temperature, fuel nitrate ratio etc. on the properties of nickel ferrite has not been reported in the literature to our knowledge. The present work is an attempt to understand the effect of varying metal nitrate to citric acid (fuel) ratio on the structural and magnetic properties of nickel ferrite synthesized by sol-gel auto combustion technique.

Experimental

The high purity AR grade ferric nitrate, nickel nitrate, citric acid and ammonia solution were used to prepare nickel ferrite. These nitrates and citric acid were weighed accurately to have proper stoichiometry proportion required in the final product. An aqueous solution containing nickel nitrate (0.1 M) and ferric nitrate (0.2 M) was prepared first and then these two solutions were mixed together and stirred for about 1 h. Citric acid was added in the mixed solution of nickel nitrate and ferric nitrate and stirred. During the stirring process liquid ammonia was added drop by drop to obtain pH of 9. The mixed solution was simultaneously heated at 60 °C for 3 to 4 h to form a sol. The transparent sol was heated at 80 °C for 2 h for removal of water. The sol turns into a viscous brown gel. The gels were prepared with different molar ratios of nitrate and citric acid (1:1, 1:2, 1:3, 1:4, 1:5). The temperature of the gel was further increased up to 120 °C, after some time combustion of the gel takes place and fine powder of nickel ferrite nano particle was obtained. The powder was dried and annealed at 500 °C for 6 h, and the same powder was used for further characterization.

The ferrite phase formation was investigated by the powder X-ray diffraction technique at room temperature using Philips X-ray diffractometer. The surface morphological studies were carried out

using scanning electron microscopy using JEOL-JSM-5600 N scanning electron micrograph (SEM).

RESULTS AND DISCUSSION

The X-ray diffraction patterns of nickel ferrite for varying metal nitrate to citric acid (fuel) ratio are shown in Fig. 1. It can be seen from figure 1 that the additional peak of $\alpha\text{-Fe}_2\text{O}_3$ was observed for 1:1 and 1:2 ratios. For 1:3, 1:4 and 1:5 ratio the XRD patterns clearly shows the reflections belonging to cubic spinel structure. Similar nature of XRD patterns was also reported in the literature [18]. The XRD patterns matches exactly with the standard powder X-ray diffraction [19] confirming the formation of single phase nickel ferrite. The intensity of the (311) peak founds to increase with increase in nitrate-fuel ratio. The XRD data was used to obtain structural parameters. The lattice constant 'a' was determined from the XRD data and the values are presented in Table. 1. It is found that the lattice constant increases with increase in metal nitrate to citric acid (fuel) ratio. The best value of lattice constant was obtained for 1:4 ratio of metal nitrate to citric acid (fuel). The increase in lattice constant can be attributed to the fact that with increasing citric acid (fuel) increases the homogeneity and reactivity.

The X-ray density 'dx' for all the samples was calculated using the formula,

$$dx = \frac{8M}{Na^3} \quad \text{g cm}^{-3} \quad (1)$$

where, M is molecular weight of the sample, N is Avogadro's number, a is lattice constant.

The values of X-ray density are given in Table 1. The X-ray density decreases with increase in metal nitrate (fuel) ratio. The decrease in X-ray density is attributed to increase in lattice constant.

The crystallite size was determined from the linewidth of the reflection of the most intense peak in XRD pattern using the Scherrer formula [20]. The values of crystallite size for various metal nitrates to fuel ratio are given in table 1. It is observed that crystallite size of the product (Nickel ferrite) get affected by the metal nitrate to citric acid (fuel) ratio. The crystallite size was obtained in nanometer range (20 to 30 nm). The minimum value of crystallite size was obtained for 1:4 ratios.

The SEM image for typical sample (1:4) is shown in Fig. 2. It is observed from SEM image that there is uniform grain growth with minimum pores. The grain size obtained from SEM images is listed in Table 1. The specific surface area was calculated from the measured diameter of the particle and density of the sample using the relation [21].

$$S = \frac{6000}{td_m}$$

Where, t is particle size and d_m is the measured density. The values of surface area are given in table 1. It is observed that surface area increases with increase in metal nitrate to citric acid (fuel) ratio. This can be attributed to decrease in crystallite size with increase in nitrate to fuel ratio.

CONCLUSIONS

Using novel auto combustion synthesis method nano-crystalline nickel ferrite samples of size less than 30 nm were obtained for various metal nitrates to citric acid (fuel) ratio. The lattice constant increases with increase in nitrate to fuel ratio. The particle size of the powder synthesized also depends on the ratio of metal nitrates to citric acid. The best values of structural and magnetic properties are obtained at 1:4 metal nitrates to citric acid (fuel) ratio.

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