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Calcium doped nickel ferrite powders prepared by sol-gel combustion method

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ABSTRACT

Calcium doped nickel ferrite powders have been prepared by sol-gel combustion technique. Metal nitrates, such as calcium nitrate, nickel nitrate and ferric nitrate, were used as the source materials and citric acid and polyvinyl alcohol were used as the burning agent and agglomeration reducing agent, respectively. The average crystallite size of the prepared ferrite was in the order of ~70- 92 nm. Due to the vast survey on calcium based ferrite materials with the existing ferrites, it was found that the research on calcium ferrite is scanty compared to other ferrite. Moreover, there is no report available on Calcium doped with nickel ferrite materials. Therefore, we report the structural studies of $Ni_{0.5}Ca_{0.5}Fe_2O_4$ synthesized by sol-gel combustion method. The structure, cubic morphology, and the identification of functional groups of the calcium-doped nickel ferrite were analyzed systematically using several analytical tools.

Keywords: *Nanocrystals; Sol-gel combustion technique; Nanoferrites; XRD.*

INTRODUCTION

Nanocrystalline material is an attractive class of materials owing to their small size which exhibit novel properties which differ from those of the bulk materials. However, Magnetism of the fine particles has drawn considerable interest in the last two decades. When particle size goes below the critical value, change in the domain structure causes a drastic amendment in their magnetic properties such as saturation magnetization and anisotropy [1]. Chemically synthesized nanomagnetic particles have drawn much attention (2-4) due to their unique magnetic properties and uniform particle size distribution. The ability to produce nanosize magnetic materials has opened new application for magnetic materials such as magnetic media for high density recording, magnetocaloric refrigeration, electromagnetic inference shielding (EMI), sensors, contrast enhancement in magnetic resonance imaging, and magnetically guided drug delivery in bio-medicine [5-10] etc.

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In recent years, good deal of attention [11-13] has been made on the processing of good-quality ferrites. Spinel ferrites are commercially important materials because they possess exceptional magnetic and electrical properties. The wet-chemical synthesis of high reactive powders has been proved to be one of the most effective routes to decrease the sintering temperature of ferrites. Several chemical methods such as co-precipitation, hydrothermal synthesis, electrochemical, pyrolysis and sol gel process have been developed [14-18] for the preparation of ferrites powders. Among these methods, sol-gel assisted combustion technique is more popular, because of simplicity and low cost.

On the other hand, many research groups have examined the effect of trivalent and divalent substitution in different ferrites to improve their structural, electrical and magnetic properties. The effects of Cr^{3+} substitution on M type barium ferrites prepared by a nitrate-citrate gel-auto combustion process were reported by Ounnunkad *et al.* [19], concluding that the saturation magnetization systematically decreases with increasing Cr concentration, whereas the coercivity increases. Arulmurugan *et al.* [20] have reported that ferrofluids having $CO_{0.5}Zn_{0.5}Fe_2O_4$ and $Mn_{0.5}Zn_{0.5}Fe_2O_4$ fine particles were prepared by co-precipitation and ball milling method. Modified synthesis technique for Mn-Zn ferrite with high magnetization for temperature sensitive magnetic fluid has been reported by Jeyadevan *et.al.* [21] and the revealed results confirmed the formation of single phase nano crystalline NiZnCu ferrites dispersed in silica matrix when the sample is annealed at 550^{o}C. The transition from the paramagnetic to ferromagnetic state is observed as the anneal temperature from 750^{o}C to 1150^{o}C were reported by Shifeng Yan *et al.* [22]. Further, based on our knowledge the preparation and characterization of Ca substituted $NiFe_2O_4$ have been found to be scanty. Therefore, in the present investigation, metal nitrates as precursors and citric acid as an oxidizing agent have been used to prepare the $Ni_{0.5}Ca_{0.5}Fe_2O_4$ using sol-gel coupled with combustion technique. The prepared $Ni_{0.5}Ca_{0.5}Fe_2O_4$ nanoparticles have been characterized employing different techniques to analyze the structure and to explore the other interesting properties.

EXPERIMENTAL

The chemicals used in the present investigation were of analytical grade (AR) with high purity of 99.99% and purchased from Sigma Aldrich, India. The same were used without any further purification. Nickel nitrate (0.5 mol), Calcium nitrate (0.5 mol), Ferric nitrate (1 mol) and Citric acid (0.5 mol) were used for sample preparation by the sol-gel combustion method [23].

Characterization

The crystalline phases of the present sample has been studied employing the powder X-ray diffraction (Philips, USA) technique using a monochromatised CuKα (1.54056 A$^{\circ}$) source. The morphology of the powders was analysed using Transmission electron microscopy (TEM) (JEOL JEM 3010) and Particle size of the $Ni_{0.5}Ca_{0.5}Fe_2O_4$ was determined from the observed TEM micrographs. The room temperature infrared spectra of nanopowders were recorded employing Fourier Transform Infrared (FTIR, SHIMADZU) from 4000 to 400 cm^{-1}.

RESULTS AND DISCUSSION

The obtained XRD pattern of the $Ni_{0.5}Ca_{0.5}Fe_2O_4$ powders is shown in Figure 1 The average crystalline size is obtained from the broadening effect of the most intense peak employing the Scherrer formula [1] as,

$$D = \frac{K\lambda}{\beta \cos\theta} \qquad (1)$$

Where, β is the full width half maximum (rad), λ the wavelength of the X-ray, θ the angle between the incident and diffracted beams (degree) and D the particle size of the sample (nm).

The X-ray diffraction pattern of $Ni_{0.5}Ca_{0.5}Fe_2O_4$ particles is shown in Figure 1 and crystalline size of the prepared ferrites are shown in Table 1. The observed results reveal the increase in calcination temperature increases the crystalline nature of the particle. The increase in calcination temperature from 300°C to 900°C reveals a further increase in nanocrystalline size (Table 1).

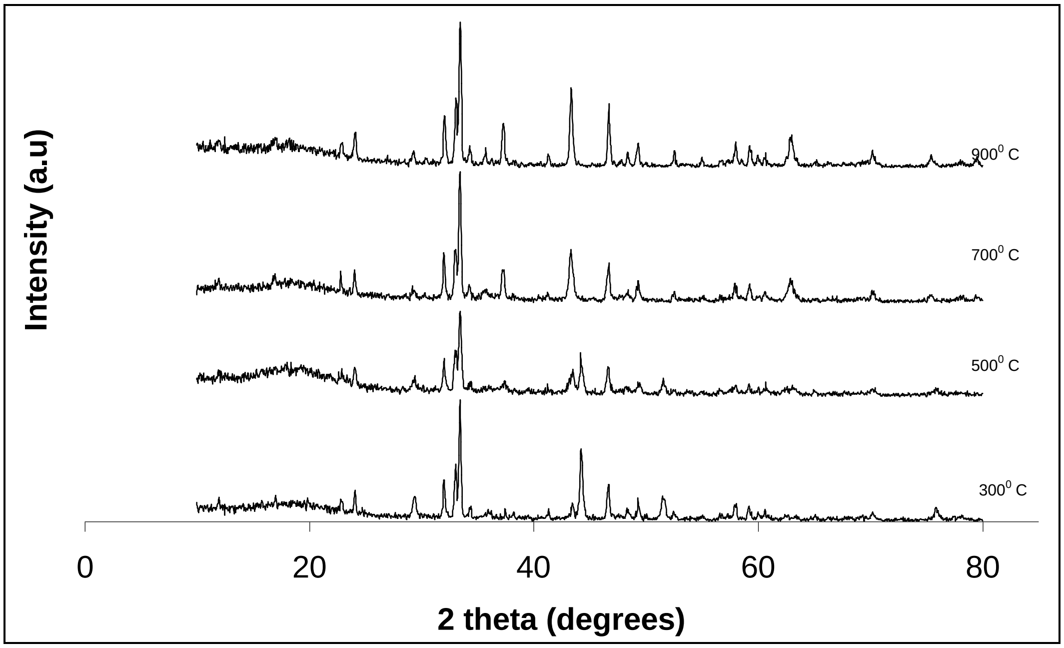

Fig.1. XRD Spectra of $Ni_{0.5}Ca_{0.5}Fe_2O_4$ nanoferrites at 300, 500, 700 and 900°C

Table.1. Variation crystal size with calcination temperature

Calcination temperature °C	Crystalline size (XRD) nm
300	69.9
500	70.2
700	80.3
900	92.7

The calcination temperature is one of the important factors which control the particle size. In the present $Ni_{0.5}Ca_{0.5}Fe_2O_4$ samples shows the enhancement in crystal size with increase in calcination temperature. An increase in crystal size with an increase in calcination temperature has been reported on Zinc ferrite, Ni ferrite systems [24, 25]. It is inferred from the above results that the sol gel combustion method is the simplest chemical route and low cost preparation method for the preparation of the nanoparticles over a wide range of particle size. The TEM photograph of sample 500°C is shown in Figure 2. The average particle size of the $Ni_{0.5}Ca_{0.5}Fe_2O_4$ was found to be ~80 nm which is in accordance with XRD results.

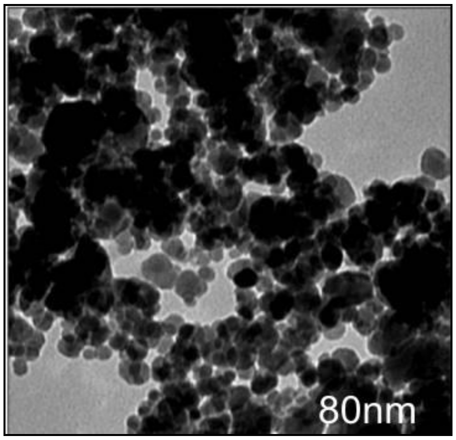

Fig.2. Transmission electron spectroscopy of $Ni_{0.5}Ca_{0.5}Fe_2O_4$ nanoferrites 500°C

The observed FTIR spectra of the $Ni_{0.5}Ca_{0.5}Fe_2O_4$ nanopowders in the wave number 4000 - 400 cm^{-1} is shown in Figure 3. The observed spectra show the characteristic peaks at 602.71, 416.60 and 403.09 cm^{-1}. The observed peak at 602.71, 416.60 and 403.09 cm^{-1} of the powders at 300°C indicates the presence of metal oxide. The formation of metal oxide at the characterization peaks at 602.71, 416.60 and 403.09 cm^{-1} on Ni ferrite [23,26] support the observation made in the present study.

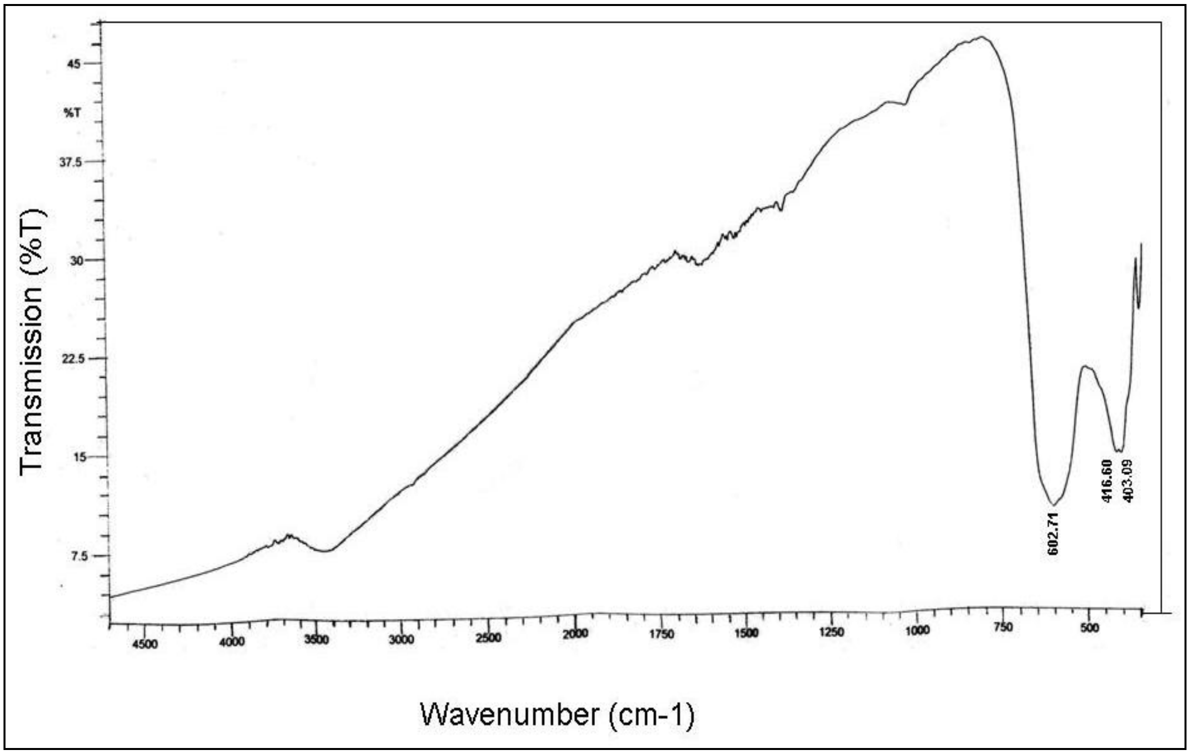

Fig. 3. Fourier Transform Infrared Spectra of $Ni_{0.5}Ca_{0.5}$

CONCLUSION

The $Ni_{0.5}Ca_{0.5}Fe_2O_4$ nanoparticles were successfully synthesized through citric acid-assisted sol gel combustion method. A wide range of $Ni_{0.5}Ca_{0.5}Fe_2O_4$ particle sizes within the nanometer scale is obtained by this method with addition of agglomeration reducing agent. An increase in calcination temperature increases the crystalline nature of the particle. Nanostructure was confirmed by XRD and TEM studies. Moreover, the same work may be extended to characterize the electrical and magnetic properties for analyzing the resourceful properties of the $Ni_{0.5}Ca_{0.5}Fe_2O_4$.

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