Citric acid as an organic complexing/fuel agent for the synthesis of Ce doped Co–Zn ferrite nanoparticles

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Abstract

Complexant organic agents can effectively chelate metal ions with varying ionic sizes. They also serve as reductant being oxidized by nitrate ions, thus working as fuel in a synthetic method named auto combustion sol-gel. However, citric acid ($C_6H_8O_7$) is most frequently used in producing in large variety of ferrites. It is inexpensive and is a more effective complexing agent than other complexant producing fine ferrite powder with smaller particle size. The spinel ferrites are unique materials exhibiting ferrimagnetic and semiconductor properties and can be considered as magnetic semiconductors. Among different ferrite materials, $Co_{0.5}Zn_{0.5}Ce_{0.05}Fe_2O_4$ with a spinel structure are attractive for the biomedical application as a result of suitable Curie temperature, magneto crystalline anisotropy, moderate saturation magnetization and super paramagnetic behavior at room temperature. The interactions between the ions, when they are substituted with various metal cations allows some tunable changes in the electrical and magnetic properties of nanoferrites. In current work, citric acid as a complexant/fuel agent was used for the synthesis of $Co_{0.5}Zn_{0.5}Ce_{0.05}Fe_{1.95}O_4$ ferrite sample based on the sol–gel auto combustion method. It is important to select appropriate complexant additives for phase formation by the auto-combustion method. The elemental analysis of the sample was carried out by using energy dispersive X-ray spectrometer (EDAX). The XRD and FT-IR studies show the formation of one spinel phase, the SEM showed the spherical nanoparticles. The magnetic properties have been measured at room temperature by a Vibrating Sample Magnetometer (VSM).

Keywords: Citric acid, Auto combustion, Sol-gel, Ferrite

1. Introduction

The spinel ferrites are unique materials exhibiting ferrimagnetic and semiconductor properties and can be considered as magnetic semiconductors [1]. The interactions between the ions in A and B sites, when they are substituted with various metal cations allows some tunable changes in the electrical and magnetic properties of nanoferrites [2]. In current work, $Co_{0.5}Zn_{0.5}Ce_{0.05}Fe_{1.95}O_4$ ferrite sample was synthesized basing on the sol–gel auto combustion method with citric acid as a complexant/fuel agent. It is important to select appropriate complexant additives for phase formation by the auto-combustion method. Complexant gents can effectively chelate metal ions with varying ionic sizes [3]. Citric acid as a convenient ligand is inexpensive and is a more effective complexing agent than other complexant producing fine ferrite powder with smaller particle size [4].

Magnetic nanoparticles have gained the great interest in recent years due to their increased use in clinical and technological applications. Ferrites can be represented by the chemical formula AB_2O_4, where A and B denote metal cations on the tetrahedral (A) and octahedral (B), respectively [5]. Among different ferrite materials, $Co_{0.5}Zn_{0.5}Fe_2O_4$ with a spinel structure are attractive for the biomedical application as a result of suitable Curie temperature, magneto crystalline anisotropy, moderate saturation magnetization and super paramagnetic behavior at room temperature [6]. Cobalt zinc ferrite has inverse spinel structure with Co^{2+} ions in the octahedral (B) sites, normal spinel structure with zn^{2+} ions in the tetrahedral (A) sites and Fe^{3+} ions equally distributed between tetrahedral (A) and octahedral (B) sites [7].

2. Experimental

In current work, $Co_{0.5}Zn_{0.5}Ce_{0.05}Fe_{1.95}O_4$ ferrite sample was synthesized basing on the sol–gel auto combustion method. The AR Grade $Fe(NO_3)_3.9H_2O$, $Co(NO_3)_2.6H_2O$, $Ce(NO_3)_3.9H_2O$, $Zn(NO_3)_2.6H_2O$ and citric acid mono hydrate ($C_6H_8O_7.H_2O$) were weighed in desired stoichiometric proportions and were dissolved in the of distilled water. The molar ratio of nitrates to citric acid was 1:1. The individual solutions were then mixed together and the pH value was adjusted to 7 by adding NH_4OH solution. Then the mixed solution was kept stirred at 80 for 1 h to transform into gel. The solution was then burnt to self-ignition to obtain a loose powder. Finally, the powder was sintered at 1000℃ for 2h.

3. Results and discussion

The XRD pattern of $Co_{0.5}Zn_{0.5}Ce_{0.05}Fe_{1.95}O_4$ nano powder was shown in Fig. 1. The diffraction peaks correspond to (220), (311), (400), (422), (333), (511), and (440) planes. All the peaks detected in the XRD patters belong to cubic spinel lattice of cobalt ferrite (JCPDS no. 22-1086) and zinc ferrite (JCPDS no. 77-0011) and in addition to desired spinel phase a minor undesired CeO_2 (JCPDS no. 08-6411) phase has been formed.

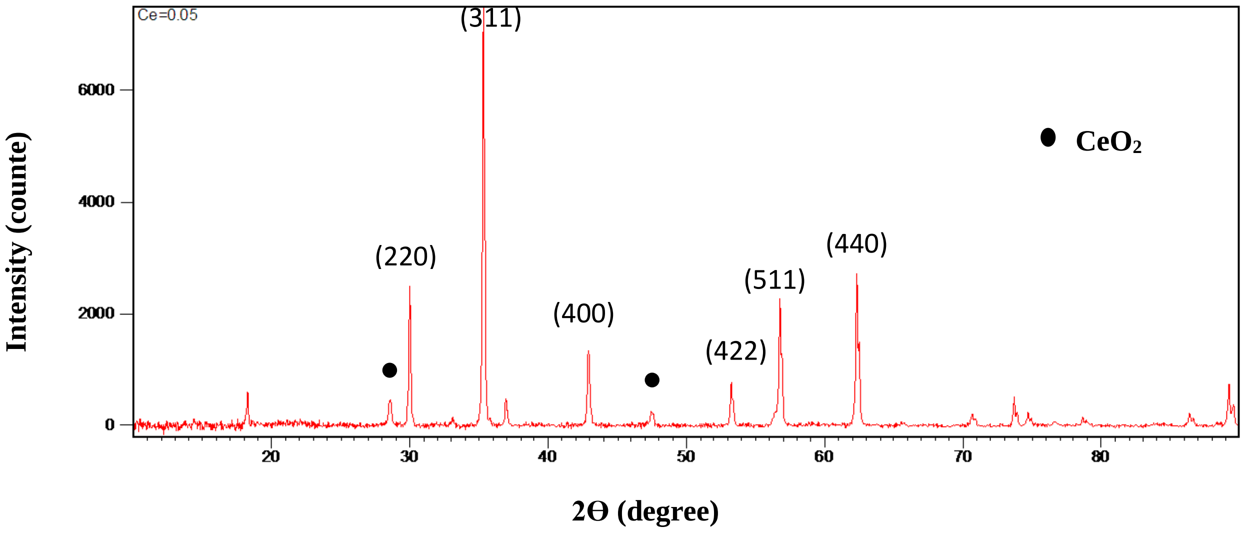

Fig. 1. XRD pattern of $Zn_{0.5}Ce_{0.05}Fe_{1.95}O_4$ ferrite sample

It can be explained that if the cobalt ferrites doped with small content ($0<X\leq0.05$), the Ce^{3+} ions would migrate either into the crystal structure or into the interstitial sites/grain boundary. As a result, the ions dissolved in the matrix and thus the solid solution formed [8]. The average crystallite size for sample has been calculated from the line broadening of the most intense peak corresponding to (311) plane of the spinel structure using the classical Scherrer equation:

$D=(0.9\ \lambda)/(\beta\cos\theta)$ [9]. The lattice constant of the sample was determined using the relation: $a_{\exp}=d_{hkl}\sqrt{h^2+k^2+l^2}$ [10]. Its values are listed in Table 1.

Table 1.

Ferrites composition	**D(nm)**	**a(Å)**
$Co_{0.5}\ Zn_{0.5}\ Ce_{0.05}\ Fe_{1.95}\ O_4$	58.4	8.423

The FT-IR transmission spectra of $Co_{0.5}Zn_{0.5}Ce_{0.05}Fe_{1.95}O_4$ is shown in Fig. 2, in 4000-350 cm^{-1}. Two frequency bands near 400 and 600cm^{-1} indicate the presence of cation–anion interactions in the octahedral and tetrahedral sites, respectively [11].

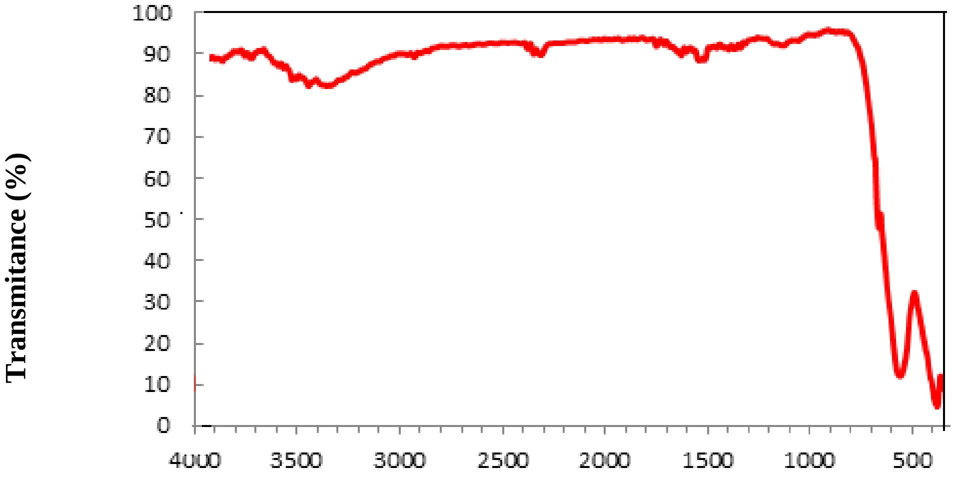

Fig. 2. FT-IR spect **Wavenumber(cm^{-1})** O_4 nano ferrite

The elemental analysis of the sample was carried out by using energy dispersive x-ray spectrometr (EDAX) and it shown in fig. 3. The EDAX result clearly shows that sample contain Ce, Co, Zn, Fe and O without any impurity.

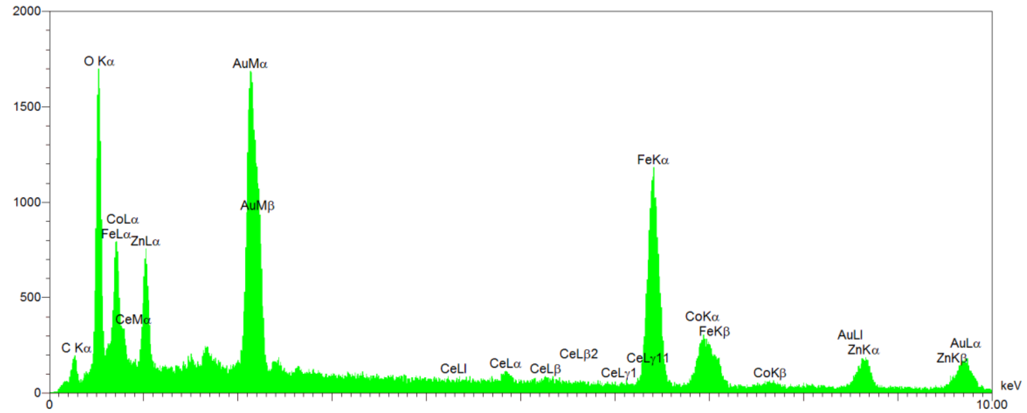

Fig. 3. Energy dispersive spectrum of $Zn_{0.5}Ce_{0.05}Fe_{1.95}O_4$ ferrite sample

FESEM images of the samples are shown in Fig. 4. As can be seen the sample has nearly homogeneous spherial nanoparticles.

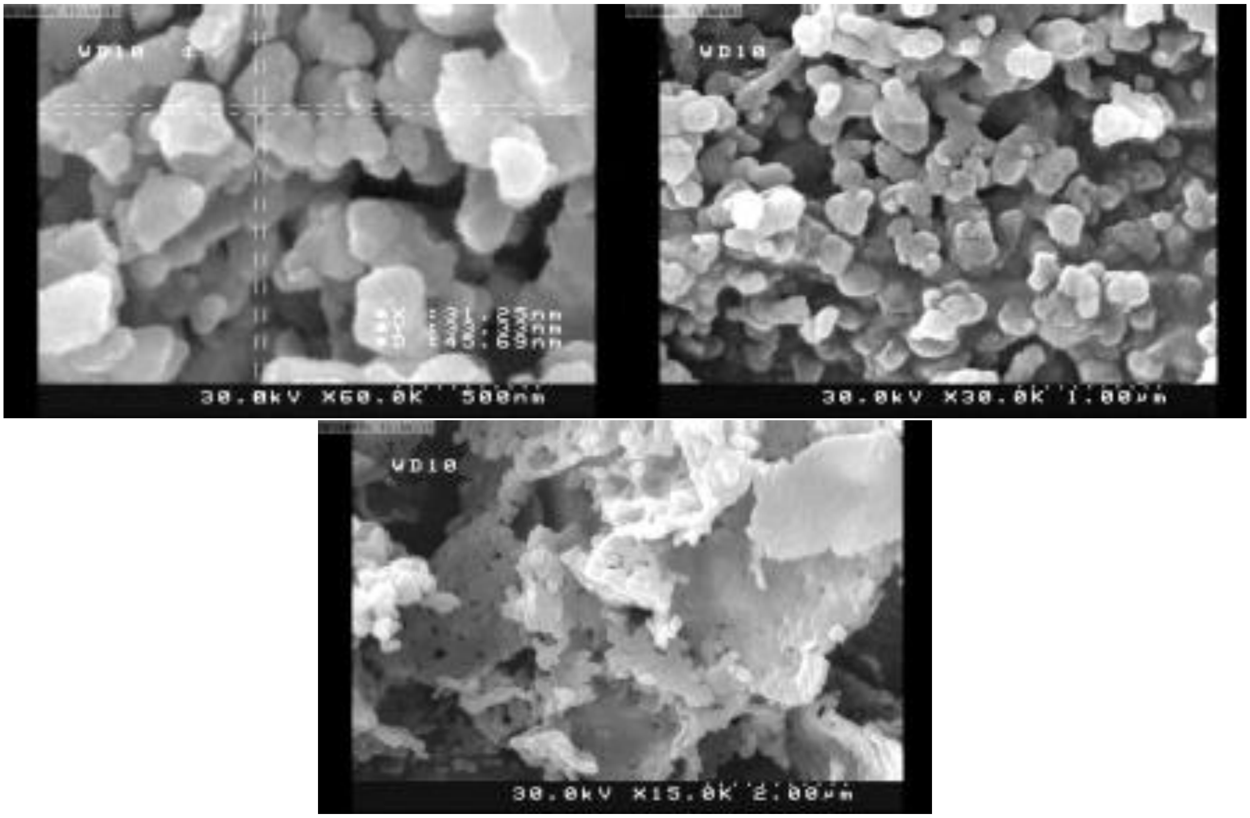

Fig. 4. FESEM micrographs of the $Zn_{0.5}Ce_{0.05}Fe_{1.95}O_4$ ferrite sample

Magnetic characterization of the particles was done using vibrating sample magnetometer (VSM), at room temperature and with maximum applied field up to 10 kOe (Fig. 5). The absence of saturation, remanent magnetization, and coercivity in the M–H curves indicate the super-paramagnetic nature of the particles. From the table it is clear that the value of Ms corresponding to ferrite nano particles is 53.076 emu/g.

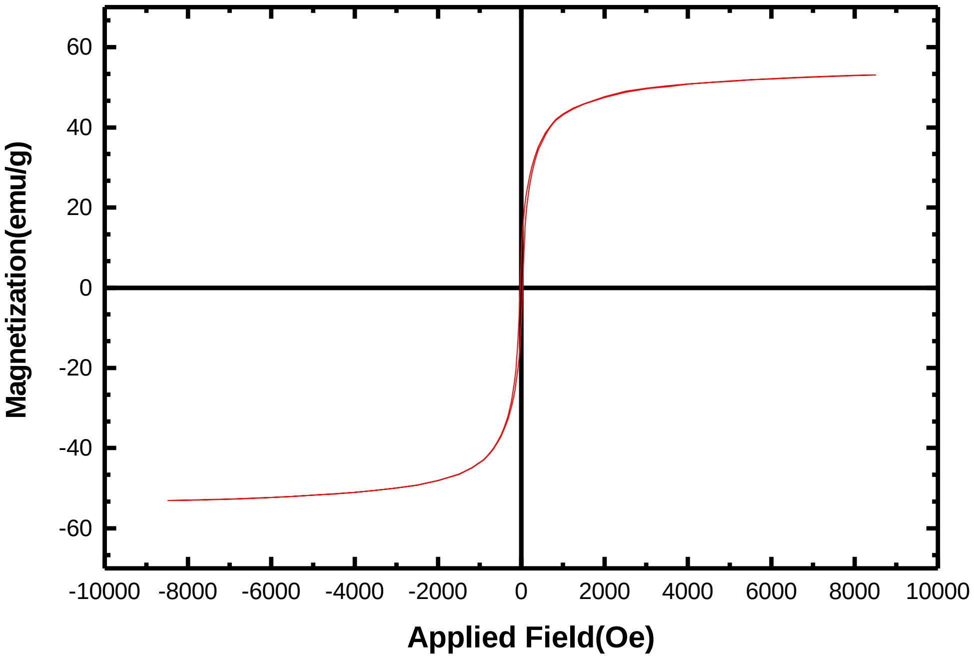

Fig. 5. Hysteresis loops of the $Co_{0.5}Zn_{0.5}Ce_{0.05}Fe_{1.95}O$ ferrite sample

The non-saturation of the magnetization also implies the presence of the single domain nnanoparticles in the super-paramagnetic state [12].

4. Conclusion

$Co_{0.5}Zn_{0.5}Ce_{0.05}Fe_{1.95}O$ ferrite nanoparticles have been synthesized using the sol–gel auto combustion method. The XRD and FT-IR studies show the formation of one main phase of spinle in all with the second phase of CeO_2 in sample(c). The SEM showed aglomerated spherial nanoparticles. The presence of Ce, Co, Zn, Fe and O elements in the ferrite sample were confirmed from EDAX measurements. The saturation magnetization of nanoferrte was 53.076 emu/g.

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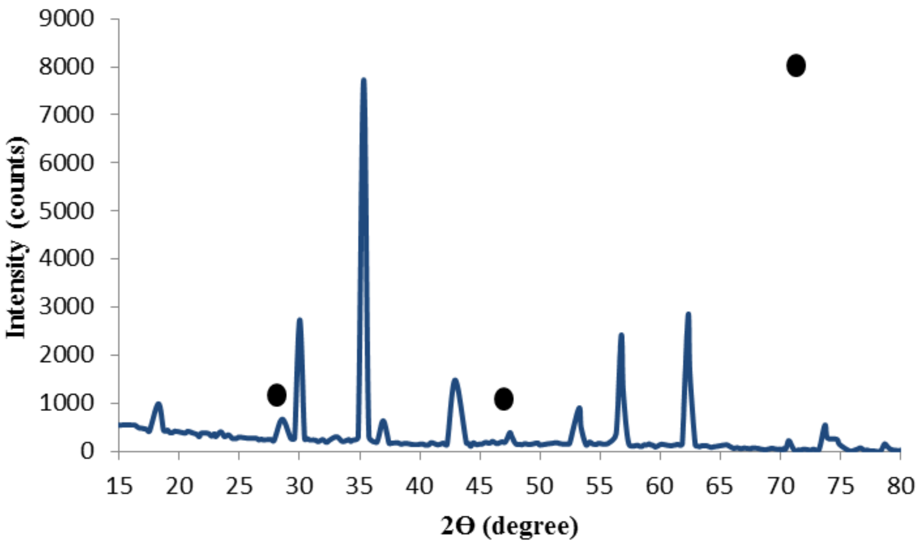

Intensity (counts)
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
15
20
25
30
35
40
45
50
55
60
65
70
75
80
2Θ (degree)
●
●
●