Influence of pH and fuels on the combustion synthesis, structural, morphological, electrical and magnetic properties of CoFe$_2$O$_4$ nanoparticles

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ABSTRACT

Nanocrystalline spinel cobalt ferrite particles are synthesized by simple combustion method using aspartic acid and glycine as fuels. The single phase cubic structure of CoFe$_2$O$_4$ is revealed through X-ray diffraction analysis (XRD). Further the Rietveld refinement confirms the formation of inverse spinel structure of CoFe$_2$O$_4$. The characteristic functional groups of Co–O and Fe–O are identified from Fourier Transform Infrared (FT-IR) analysis. Uniform distribution of of nearly spherical particles with the size range of 40–80 nm is identified through field emission scanning electron microscope (FESEM) images. The calculated DC conductivity is 1.469×10^{-7} and 2.214×10^{-8} S cm^{-1}, for CoFe$_2$O$_4$ synthesized using aspartic acid and glycine, respectively. The dielectric behavior obeys the Maxwell–Wagner interfacial polarization. The ferromagnetic behavior of CoFe$_2$O$_4$ is identified using VSM analysis and the calculated coercivity is 27 Oe and saturation magnetization is 68 emu/g.

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1. Introduction

Generally, synthesizing nanosized materials is an interesting and challenging area of research for the technological applications. Oxide spinels (AB$_2$O$_4$), is an important class of materials, which are widely investigated in recent years [1]. Though it seems to be simple in structure but it exhibits complex disordering phenomena due to its two different cations of A and B. Hence the cation distribution is responsible for many of its physical [2], chemical [3], as well as it electrochemical [4] properties. Studies on thermodynamics of cation distribution have a long standing history over many decades and an extensive report is seen in literature [5]. Consequently, the degree of cation inversion makes a significant difference in its magnetic properties. Generally the spin magnetic moments of the unpaired 3d electrons of the transition metal cations and oxygen atoms are coupled by the super exchange interaction which are are responsible for the existence of magnetic properties.

Among the transition metal ferrites, MFe$_2$O$_4$ (M = Co, Zn, Cd, Ni, Mn), CoFe$_2$O$_4$ is our interest and has an inverse spinel structure, where the Co^{2+} ions are occupied in the octahedral site and Fe^{3+} ions are equally distributed in both tetrahedral and octahedral sites [6]. Exclusively due to its strong anisotropy, high coercivity, moderate saturation magnetization, low cost, good mechanical hardness and chemical stability allows CoFe$_2$O$_4$ to be a potential candidate in electronic industry. Also it has been used for anticorrosive pigments for ceramic application, magnetic recording media, biomedicine, microwave devices, magnetic resonance imaging, electrodes for Li-ion batteries and supercapacitors [7].

There are many reports available regarding the synthesis of CoFe$_2$O$_4$ including sol gel [8], chemical co-precipitation [9], solvent casting [10], hydrothermal synthesis [7] and microwave assisted combustion [11], etc., since the synthesis method is also influences on the cation distribution, that provides different physico-chemical properties. Hence it is mandatory to find the suitable tailor made method to tune the desired properties for the specific applications. Herein we report the synthesis of nanosized CoFe$_2$O$_4$ particle through cost-effective, simple and efficient combustion synthesis method. Even though, the scarce amount of work has been reported for the synthesis of CoFe$_2$O$_4$ by combustion method using different fuels of alanine [12], glucose [13] and so on. For the first time, aspartic acid is used as an organic fuel as well as the

chelating agent for the synthesis of $CoFe_2O_4$ nanoparticles by combustion method. In addition, $CoFe_2O_4$ was prepared at different pH conditions (pH 5, pH 7 and pH 10) and studied their electrical, dielectric and magnetic properties in detail. Further the above said improved properties are compared with the materials prepared by using conventional fuel i.e., glycine at all the above pH conditions. The theoretical thermodynamic parameters are also calculated to receive the adiabatic flame temperature.

2. Experimental methods and materials

2.1. Synthesis of $CoFe_2O_4$ nanoparticles

All the precursors used for this synthesis were high purity chemicals obtained from MERCK. For a typical synthesis, stoichiometric amounts of $Co(NO_3)_3 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ were dissolved in a minimum amount of double distilled water. Subsequently, the desired amount of aspartic acid and poly ethylene glycol 400 were added. Here, the aspartic acid acts as a chelating agent which produced a homogenous sol. Subsequently, the mixtures were allowed for continuous stirring in a quartz crucible for 10 min. After that the solution pH was changed to 5, 7 and 10 individually using ammonia solution. Then the reactant mixtures were dried at 80 °C with continuous stirring for 2 h, and obtained a solid mass. Finally, the obtained solid mass was kept at 200 °C in an electric furnace for the combustion reaction. During combustion, a voluminous amount of fumes was evolved due to the exothermic reaction. As a result, the foamy powder of $CoFe_2O_4$ was obtained, which further calcined at 700 °C for 1 h in air atmosphere to improve the crystallinity. Hereafter, the prepared materials are called as CA5, CA7 and CA10 with respect to their fuel (A-aspartic acid) and pH (5, 7, 10). The similar procedures were repeated for the preparation of $CoFe_2O_4$ using glycine (G) as fuel and the samples were named as CG5, CG7 and CG10. Overall, this report deals with the effect of two different fuels (aspartic acid and glycine) and three different pH conditions (5, 7 and 10) on the synthesis of $CoFe_2O_4$ particles.

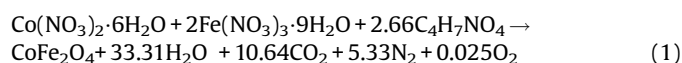### 2.2. Physicochemical characterization techniques

The crystal structure phase determination and phase purity of the prepared samples were investigated by X-ray diffraction analysis (XRD) on a Bruker D8 Advance with Cu K_α as a radiation source with the step size of 0.05. Presence of functional groups was identified through FT-IR spectroscopy of Bruker Tenser 27. The morphology of the prepared particles was revealed through F E I Quanta FEG 200 – field emission scanning electron microscope. The electrical properties of these materials were analyzed through AC impedance analyzer of Hioki 3532 Hitester. For conductivity measurements, the powder was pressed into 1 cm diameter pellet with 0.73 mm thickness at a pressure of 150 kg/cm² under identical conditions. The pellet was then sintered at 700 °C in muffle furnace for 1 h. For better ohmic contact silver paste was applied to both surfaces of the pellet before being sandwiched between two electrodes of sample holder. Furthermore, the room temperature isothermal magnetization data is taken using VSM (ADE Technologies, USA).

3. Results and discussion

3.1. Combustion reactions: theoretical analysis

The combustion synthesis is based on the thermochemical concepts used in propellant chemistry [14]. Fuels play a significant role in the formation of product and many organic compounds have been used as fuel. In the present work, aspartic acid is used as a fuel due to its high reducing power (total valencies: +15). Using thermodynamic data [15], the various chemical reactions are arrived for the synthesis of $CoFe_2O_4$ nanoparticles and are given in Table 1. Table 2 shows the exothermic (Eq. (R1)) and decomposition reactions (Eqs. (R2) and (R3)) of aspartic acid and the individual metal nitrates. Eq., RS2 = RS1 + mR1 (Table 2) gives the overall steps of the reactions. To occur the reaction, RS2 at 25 °C, $m = 3.1998$ mol of aspartic acid is needed on the basis of enthalpy change ($\Delta H°_{RS2} = 0$). This amount of aspartic acid provided the necessary energy to complete the decomposition reaction with the evolution of byproduct gases such as $24H_2O$, $6N_2$, $13CO_2$, $15O_2$, $11H_2$, as predicted by reaction RS2. Practically this temperature is not sufficient to complete the reaction. Hence the direct use of propellant chemistry, with the metal nitrates in 1:2 molar ratio, to determine the aspartic acid needed to balance the total oxidizing and reducing valencies in the mixture of oxidizer and fuel leads to $(-10 + 2(-15) + n(15)) = 0$. It is well known that the nature of combustion product is strongly influenced by the oxidant to fuel ratio. Hence the stoichiometric composition of the redox mixture, required only $n = 2.66$ mol of aspartic acid to provide the maximum energy of the reaction. The stoichiometric equation is given in the Eq. (1),

$$Co(NO_3)_2 \cdot 6H_2O + 2Fe(NO_3)_3 \cdot 9H_2O + 2.66C_4H_7NO_4 \rightarrow$$
$$CoFe_2O_4 + 33.31H_2O + 10.64CO_2 + 5.33N_2 + 0.025O_2 \qquad (1)$$

The enthalpy of formation $(\Delta H_f)_{reactant}$ of reactant and product is -2717 kcal/mol and -3178 kcal/mol, respectively. The heat of combustion reaction is determined by using following (Eq. (2))

$$\Delta H_{combustion} = (\Sigma \Delta H_f)_{product} - (\Sigma \Delta H_f)_{reactant}$$
$$= -3178 - (-2717) = -461 \text{kcal/mol} \qquad (2)$$

Subsequently, the adiabatic flame temperature is calculated using the following Eq. (3),

$$\Delta H_{combustion} = \int_{298}^{T_{ad}} (\Sigma n C_p)_{products} dT \qquad (3)$$

Here n is the number of moles of a reaction product, T_{ad} is the adiabatic flame temperature and C_p represents the specific entropy of a system. Hence the calculated adiabatic flame temperature is 994 K. Using the same procedure, the calculated heat of combustion and adiabatic flame temperature for glycine used $CoFe_2O_4$ is -447 kcal/mol and 1026 K, respectively. Overall, when compared with glycine, less amount of aspartic acid is sufficient and comparatively low temperature is sufficient to synthesize the $CoFe_2O_4$ nanoparticles and this may be due to the high value of heat of combustion. Hence the amino acid i.e. aspartic acid may enhance the physical and chemical properties of the synthesized

Table 1
Thermodynamic data used to calculate the adiabatic temperature.

Compound	$\Delta H_f°(25 °C)$ (kcal mol⁻¹)	C_p(cal mol⁻¹ K⁻¹)
$Co(NO_3)_2 \cdot 6H_2O(c)$	−528.49	–
$Fe(NO_3)_3 \cdot 9H_2O(c)$	−785.2	–
$C_4H_7NO_4(c)$	−232.47	–
$CH_2NH_2COOH(c)$	−126.31	–
$CoO(c)$	−56.858	
Fe_3O_4	−266.9	35.19
$Fe_2O_3(c)$	−198.5	24.82
$CoFe_2O_4(c)$	−252	$10.34 + 0.00274T$
$CO_2(g)$	−94.05	35.36
$H_2(g)$	0	–
$H_2O(g)$	−57.79	$7.2 + 0.0036T$
$N_2(g)$	0	$6.5 + 0.00100T$
$O_2(g)$	0	$5.92 + 0.00367T$