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Synthesis and characterization of calcium ferrite nanoparticles by solution combustion method

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Abstract

The current paper has focussed on the synthesis and characterization of calcium ferrite nanoparticles by solution combustion method. Calcium ferrite nanoparticles were prepared by a solution based method using calcium chloride ($CaCl_2$), ferrous sulphate ($FeSO_4$), dl–Alanine and sodium hydroxide (NaOH) as a precipitant and the obtained precipitation was calcined under 500 °C for 4 hours. The resulting material was characterized by using X–ray diffractometry, Scanning electron microscopy, FTIR Spectroscopy and UV–Vis spectroscopy. The magnetic characterization was done by using a vibrating sample magnetometer. The electrical conductance, salinity and total dissolved solid measurements of the prepared nanoparticles were conducted. From PXRD results the calculated crystalline size is 12 nm. SEM micrograph reveals the formation of spherical structures. The FTIR spectrum confirms the Ca–O and Fe–O bonds in the sample. The VSM analysis reveals that the particle shows superparamagnetism.

Keywords: Calcium ferrite, Nanoparticles, Combustion, Super paramagnetism

1. INTRODUCTION

Ferrites are iron based oxides with technologically fascinating magnetic properties, making them a prominent category in magnetic materials.The behaviour of ferrite compounds depends on the method of preparation as well as the purity, crystallinity and magnetic properties of the input materials [1]. Ferrites are divided into three families; spinels, hexagonal ferrites and garnets. Spinel type oxides with general formula AB_2O_4 are the most widely used in the family of ferrites [2].The ferrite particles in nano–regime with significant change of physical properties provide more advantages over the bulk ferrites. In the nano–regime ferrites were found to have undergone changes in magnetic properties due to superparamagnetism and surface spin effects until the stable magnetism occurs below the blocking temperature [3,4].

The $CaFe_2O_4$ type structure includes edge and corner sharing BO_6 octahedral, constituting a very distinctive network similar to the one formed in pervoskite related compounds, this structural network suggests that interesting physical properties may exist in the $CaFe_2O_4$ compounds, where B–site atoms are transition metal magnetic elements, such as high–T_C superconductivity in cuprates, quantum magnetic characters in ruthenates, strongly correlated features in magnetates [5]. In comparison with the other ferrites such as $MnFe_2O_4$, $NiFe_2O_4$, $ZnFe_2O_4$, $CoFe_2O_4$ and $CuFe_2O_4$, calcium ferrite has a significant advantages; it is biocompatible and eco–friendly due to the presence of Ca^{2+} instead of heavy metals [6].Calcium ferrites have extensive applications in the optical memory devices [7], magnetoplumbite structure [8,9] and steel making industries [10,11]. Also it has considerable applications in information storage devices, magnetic bulk cores, magnetic fluids, microwave absorbers, catalysts and medical diagnostics [2,3,12].

Combustion synthesis has emerged as an important technique for the synthesis and processing of advanced ceramics, catalysts, composites, alloys, intermetallicand nanomaterials. In this method, the exothermicity of the redox chemical reaction is used to produce useful materials. Combustion synthesis processes are characterized by high temperatures, fast heating rates and short reaction times. These features make combustion synthesis an attractive method for the manufacture of technologically useful materials at lower cost compared to conventional ceramic processes [13,14].

2. MATERIALS AND METHODS

Calcium chloride ($CaCl_2$), Ferrous sulphate ($FeSO_4$), Sodium hydroxide (NaOH), dl–alanine and absolute ethanol (99.9%). Calcium chloride and ferrous sulphate were purchased from SD fine chemicals. All other chemicals were of analytical grade. All the aqueous solutions were prepared using distilled water.

The first solution 0.2 M $CaCl_2$, 0.4 M $FeSO_4$ and 0.2 M dl–alanine was dissolved in 250 mL of distilled water and the second solution was prepared by 3M NaOH pellets in 250 mL distilled water. The second solution was added drop by drop with continues stirring on magnetic stirrer. The obtained particle solution was taken in the condenser and boiled at 100^0C temperature for about 2 hours then the hot solution was filtered using Whatmann filter paper (G–41) and dried at 100 °C in a hot air oven for about 1 hour, then obtained powder was washed with ethanol 3–4 times to remove the impurities present in the $CaFe_2O_4$ nanoparticles.

Solution combustion derived product was characterised by PXRD. Powder X–ray diffraction patterns were collected on X'PERT– PRO– PHILIPS X–ray Diffractometer with CuKα radiation with diffraction angle range $2\theta = 20°– 80°$ operating at 40 kV and 30 mA. TheFT–IR studies have been performed on a Shimadzu DR–43S FTIR Spectrophotometer with KBr pellet technique in the frequency range 4000– 400 cm^{-1}.The UV–Vis spectra of the prepared calcium ferrite nanoparticles were recorded on Perkin Elmer λ25 UV–Vis Spectrophotometer. The Product was morphologically characterized by SEM analysis which was performed on a JEOL Model JSM–6390LV electron scanning microscope.The VSM analysis of the prepared $CaFe_2O_4$ nanoparticles were done on Lakeshore VSM 7410and the conductance were measured on Thermoscientific Orion 5 Star.

3. RESULTS AND DISCUSSIONS

The calcium ferrite nanoparticles are prepared by solution combustion method and its properties were characterized by Powder XRD, FT–IR spectroscopy, UV–Vis spectroscopy, Scanning electron microscopy and VSM analysis.

The crystalline size of the prepared calcium ferrite nanoparticles was obtained from PXRD results. Infrared spectra give the different vibrational modes present in the sample. The optical property can be obtained from UV–Vis absorption spectrum. The surface morphology of the prepared nanoparticles can be studied by SEM micrographs. VSM analysis gives the magnetic properties of the

calcium ferrite nanoparticles. Also the electrical conductance, salinity and TDS measurements of the prepared nanoparticles were conducted.

3.1. PXRD studies for phase formation and crystalline size

The formation of nanocrystalline phase of prepared sample was confirmed by PXRD measurements. The XRD pattern of the obtained calcium ferrite nanoparticle is shown in Figure 1. All peaks can be well indexed to the structure of calcium ferrite (matched with JCPDS PDF No 72– 1199) with highly crystalline nature. All the diffraction peaks can be indexed to (220), (320), (040), (131), (311), (331), (401), (520), (260), (600), (170), (022) and (042) reflections. The crystalline size is calculated from the full width at half maximum (FWHM) of the diffraction peaks using Debye Scherer's formula method [15] using the following equation.

$$d = \frac{k\lambda}{\beta\cos\theta}$$

Where'd' is the average crystalline dimension perpendicular to the reflecting phases; 'λ' is the X– ray wavelength, k is Scherer's constant (0.94). '$\boldsymbol{\beta}$' is the full width at half maximum (FWHM) intensity of a Bragg reflection excluding instrumental broadening and '$\boldsymbol{\theta}$' is the Bragg's angle. Here (040) reflection has maximum intensity. Therefore, full width at half maximum of (040) reflection is considered as $\boldsymbol{\beta}$. The calculated crystalline size of the sample is found to be 12 nm.

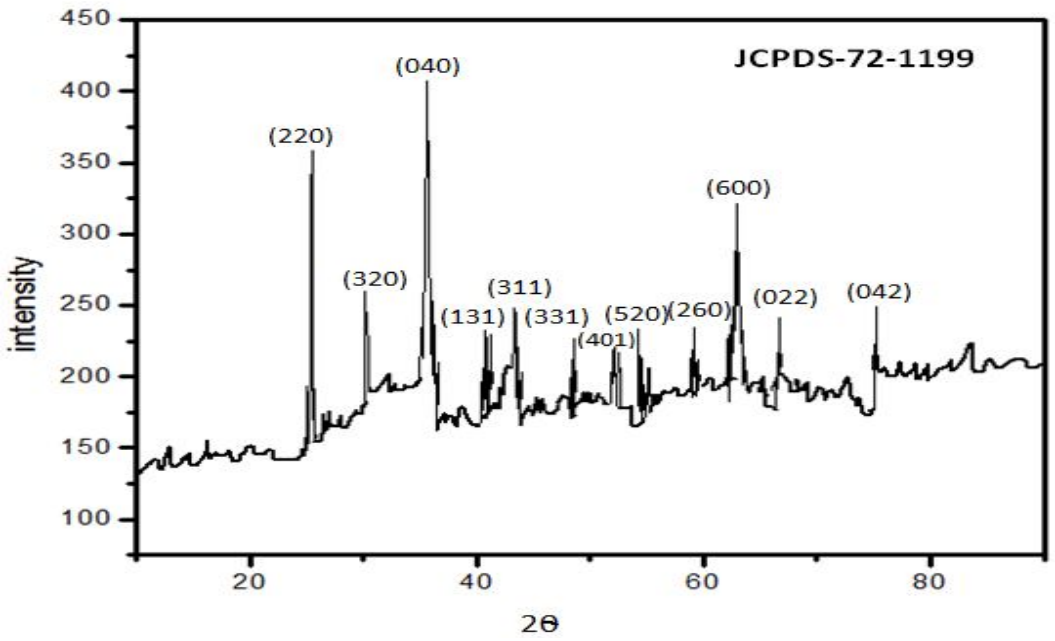

Fig. 1: XRD pattern of the obtained calcium ferrite nanoparticle

3.2. FT–IR spectroscopic studies

FTIR spectroscopy is an imperative vibrational technique to identify and construe the different bond formation in the material. The FTIR spectrum of calcium ferrite nanoparticles recorded in the range of 4000–400 cm^{-1}. The bands at 420 cm^{-1}, 557 cm^{-1} and 590 cm^{-1} correspond to the stretching vibrations of Ca–O & Fe–O bonds. The bands at 1138 cm^{-1}, 1163 cm^{-1} corresponds to the stretching vibrations of C–O [16,17].

3.3. UV–Vis spectroscopy studies

In order to determine the optical property, the UV–Vis spectrum was recorded. The sample shows a strong absorption peaks (λ_{max}) at 262 nm in the UV region and two absorption bands at 364 nm and 463 nm in the visible region. This can be attributed to photo excitation of electron from valence band to conduction band.

3.4. Morphological analysis

Figure 2 shows SEM micrographs of $CaFe_2O_4$ nanoparticles. The micrographs revealed that the particles are spherically agglomerated having uniform size and distribution. Due to this particle size cannot be measured and so it can be found out from Transmission Electron Microscopy TEM analysis.

The agglomeration of $CaFe_2O_4$ was caused by the high surface energy and magnetic dipole interaction between ferrite particles [18]. The particles are having large number of voids due to the release of gaseous products.

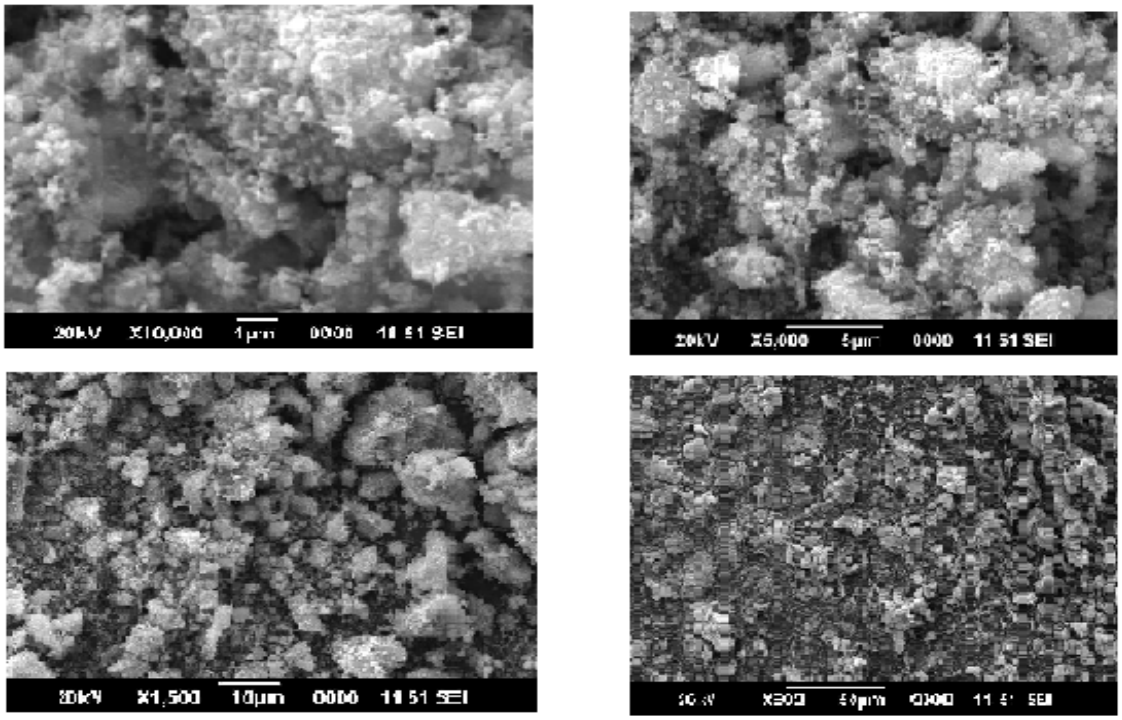

Fig.2: SEM micrographs at different magnifications

3.5 Magnetic characterization based on VSM

The hysteresis curve of the synthesized $CaFe_2O_4$ nanoparticles was measured using a VSM (Vibrating sample magnetometer) at room temperature (Fig.3). It is apparent from the figure that the magnetization of calcium ferrite nanoparticles results in high superparamagnetic behaviour at room temperature. The magnetic saturation (Ms) value of 1.236 emu/g is calculated per gram of the sample at room temperature. The coercivity (Hci) value is 8.73 G. Superparmagnetism is a form of magnetism, which appears in small ferromagnetic or ferromagnetic nanoparticles [19]. Superparamagnetism occurs in nanoparticles which are single domain, ie; composed of a single magnetic domain. This is possible when their diameter is below 3–50 nm, depending on the materials [20].

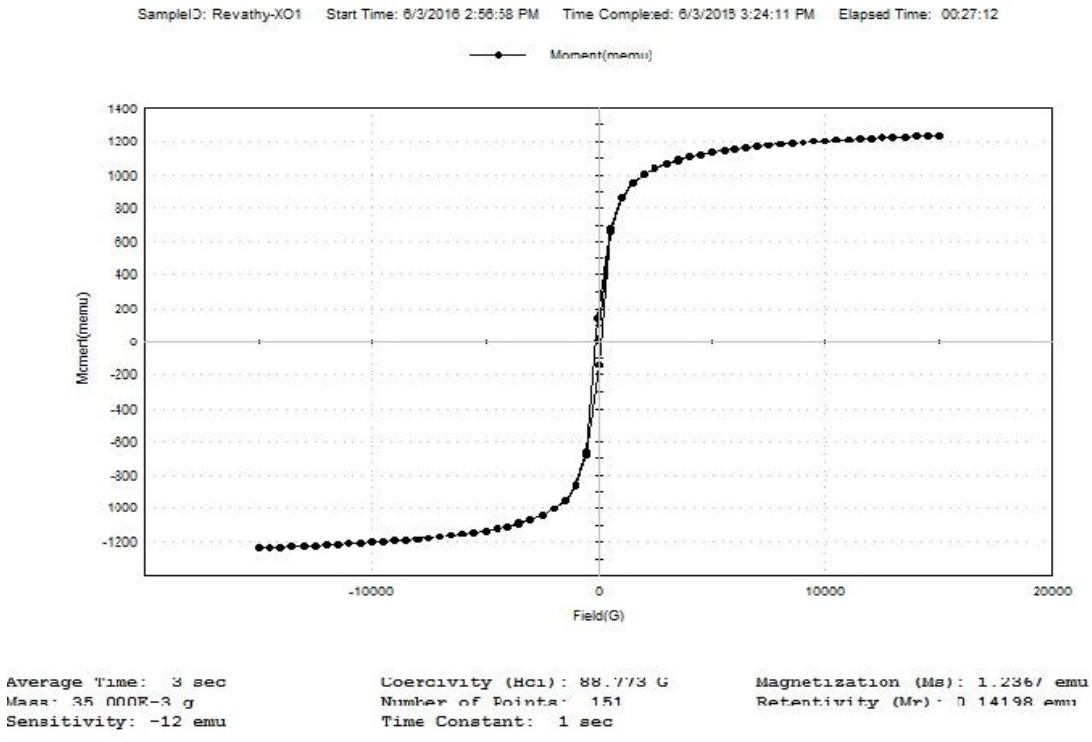

Fig. 3: VSM of $CaFe_2O_4$ nanoparticles

3.6. Measurement of Electrical conductance, salinity and TDS

Calcium ferrite clearly indicates that they are highly clustered, compact have flake like morphology and well–connected grains. Some of the particles are in spindle like shape with well–connected grain to each others. The conductivity of calcium ferrite nanoparticle is found to be 2.8 μScm^{-1}. The low electrical conductivity of calcium ferrite and high dielectric constant can be utilized in microwave materials [21].

Salinity is a measure of all the salts dissolved in water [22]. Salinity is usually measured in parts per thousand (ppt). The salinity of calcium ferrite nanoparticle is 0 ppt. Thus it is insoluble in water.

Total dissolved solids (TDS) is the measure of the combined content of all inorganic and organic substances contained in a liquid in molecular, ionized or micro–granular suspended form [23,24]. The two principal methods of measuring total dissolved solids are gravimetric analysis and conductivity. The TDS of prepared calcium ferrite nanoparticle is 1 mg/L; it is not a health hazard.

4. CONCLUSIONS

$CaFe_2O_4$ nanoparticles were successfully prepared by the simple solution combustion method using $FeSO_4$, $CaCl_2$ and dl–alanine. Powder XRD results shows that the synthesized product is well matched with JCPDS file no: 72–1199. The average crystalline size is 12 nm which is calculated from Debye–Scherer's formula. The FT–IR spectrum confirms the Ca–O and Fe–O bonds in the sample. The VSM analysis of the prepared nanoparticles revealed their superparamgnetic behaviour. The electrical conductance of the sample is found to be 2.8μScm^{-1}. SEM micrographs reveal that the particles are spherically agglomerated.

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