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Exploring structural and magnetic properties of nanocrystalline iron oxide synthesized by autocombustion method

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ABSTRACT

The nanocrystalline Fe_2O_3 is synthesized by solution autocombustion method using glycine as a fuel. The Rietveld refinement results confirm that the as prepared powder is a mixture of Hematite (α-Fe_2O_3, 80.50 wt%) and Maghemite (γ-Fe_2O_3, 19.50 wt%) phases and annealed (1000 °C for 5 h) powder is a single hematite phase of Fe_2O_3. The A_{1g} symmetry bands are observed at 227 and 502 cm^{-1} and E_g symmetry bands are observed at 293, 411, and 611 cm^{-1} in hematite phase of Fe_2O_3. Chemical composition and valence state of the samples was confirmed using XPS studies. It is found that samples are sub-stoichiometric and broadening in the Fe 2p doublet is due to the multiplet splitting effects evidencing unpaired valence electrons. ^{57}Fe Mössbauer spectroscopy analysis was used to further characterize the samples and confirm stoichiometry. Both the samples exhibit magnetically hyperfine split spectra with some special features. The annealed sample indicates the presence of only tetrahedral and octahedral site cations in hematite. The magnetic properties of the samples were studied by using *M–H* hysteresis curves. The saturation magnetizations of as prepared and annealed samples are 55.22 and 6.36 emu/g, respectively. Annealed sample exhibited larger value of coercivity (1065.6 Oe) and squareness (0.50) compared to the as prepared one (229.25 Oe, 0.28 respectively).

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1. Introduction

Iron (III) oxides are geologically, technically and archeologically important compounds. The existence of amorphous Fe_2O_3 and four polymorphs (α, β, γ, and ε) has been established [1]. In recent years, these materials have attracted wide attention of the researchers due to their potential applications in various fields such as photocatalysis, gas sensors, magnetic sensors, paint and for PEC cells [2–6]. Fe_2O_3 is spinel-type ferrite and is one of the important oxides of iron with high coercivity, moderate magnetization and very high magnetocrystalline anisotropy. It is being investigated as an alternative ceramic material for developing novel magnetostrictive smart materials [7]. Recent studies on Fe_2O_3 have shown that it can be a suitable material for developing new technologies in the areas of strategic importance. Mesoporous α-Fe_2O_3 nanostructures were used for highly sensitive gas sensors and high capacity anode materials in Lithium ion batteries [6]. Variety of methods has been used to synthesize Fe_2O_3 powders, such as ceramic [8], co-precipitation [9], solid state combustion [10], and solution combustion [11]. Among these, solution autocombustion synthesis has emerged as an attractive technique for the production of homogeneous, high purity and crystalline powders [11]. The process is carried out at a significantly lower temperature than the conventional synthesis methods, requiring shorter time and also using less amount of external energy [12]. Nanocrystalline iron oxide containing hematite and magnetite phases was synthesized by solution combustion process [13]. Combustion synthesis of Fe_3O_4 and their properties were discussed in relation to reaction atmosphere and fuel used [14]. The effect of the fuel nature and reaction atmosphere on the synthesis of maghemite and hematite by the combustion method was investigated [15,16].

Magnetism is one of the important properties of the iron oxides. The order of magnitude of magnetism is greatly influenced by the composition of the samples and also it depends on the type of preparation method. Motivated by these objectives, attempt has been made to study structural, chemical, compositional and magnetic properties of the nanocrystalline Fe_2O_3 powders synthesized by solution autocombustion method.

2. Experimental

Samples of Fe_2O_3 were synthesized by the solution combustion synthesis method. The stoichiometry was calculated on the basis of total oxidizing and reducing valencies of oxidizer (O) and fuel (F), which serves as a numerical coefficient so that the equivalence ratio, i.e. Φ_e (O/F), becomes unity and the heat released is at its maximum. The aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O$ (Thomas Beaker, 99%) was taken in a 1000 cc beaker. Then stoichiometric solution of glycine (Thomas Beaker, 99.7%) was added into it to form the redox mixture for the combustion process (O:F molar ratio 1:1.66). The resultant solution was then dehydrated slowly on a hot plate with continuous stirring until the viscous gel was formed. On further heating, the temperature of the gel increased and at a certain temperature auto-ignition of the black and fluffy gel took place with evolution of gases. During ignition smoke is produced and the products left behind are voluminous and fluffy loose powder. The resulting powder was ground for 30 min and annealed at 1000 °C for 5 h in programmable furnace.

Thermo gravimetric analysis (TGA) of as prepared powder was carried out for determination of decomposition temperature using TA Instruments model SDT Q600 for which powder was heated at the rate of 10 °C per minute in air. The structural properties were studied by a Bruker D2-Phaser X-ray diffractometer using Cu Kα radiation (λ = 1.5405 Å) in the span of 20–80°. The Rietveld powder structure refinement analysis [17] of X-ray powder diffraction data of as prepared and annealed Fe_2O_3 samples was carried out. The Rietveld program MAUD 2.45 [18] was used to refine the structural and microstructural parameters through a least-squares method. The peak shape was assumed to be a pseudo-Voigt function with asymmetry. Initially the positions of the peaks, their integrated intensity and background function parameters were manually tuned to have better resemblance between observed and simulated powder diffraction patterns. This set the best point for refining the structural parameters. The Marquardt least-squares procedures were adopted for minimization the difference between the observed and simulated powder diffraction patterns and the minimization was carried