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Influence of solvothermal growth condition on morphological formation of hematite spheroid and pseudocubic micro structures and its magnetic coercivity

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ABSTRACT

Influence of solvothermal growth condition on morphological formation and population of defects of hematite spheroid and pseudocubic micro structures and its magnetic properties were studied. Spheroid shaped crystals with different size were obtained from growth solution made of methanol, methanol-water, propanol and pseudocubic crystallites with dimension of 1.281 μm size were obtained with propanol-water solution combination at a growth temperature of 200 °C. UV absorption and magnetic properties of spheroid and pseudocubic micro structures were size and shape dependant. Spheroid shaped sample grown from precursor solution made of methanol gives intense UV absorption peaks at 360 nm and high coercivity (5.23 KOe) at room temperature. Reduction in magnetic coercivity and remanence of all samples at 5 K with respect to 300 K is attributed to antiferromagnetic nature of hematite with spheroid and pseudocubic morphology. High coercivity (6.2 KOe) at room temperature was observed from micro pseudocubic sample grown with propanol-water combination which is contributed to high aspect ratio, inter particle interaction and crystalline defects.

1. Introduction

Hematite (α-Fe_2O_3) is a corrosion resistive, thermodynamically stable n-type semiconducting magnetic material which is suitable for gas sensing [1], water splitting [2], magnetic recording [3], drug delivery [4] and hyperthermia treatment [5]. Hematite possess three critical temperatures; Neel, Morin transition and the blocking temperatures [6], consequently its magnetic properties are size and shape dependant [7,8]. Low magnetic coercivity of the order of 156 and 92 Oe are reported in star like and urchin like hematite structures [9,10]. Relatively higher magnetic coercivity is observed in mesoporous hollow micro spheroid, elliptic, pomegranate, prismatic shaped one which are 2239, 4539, 4350, 5027 Oe respectively [4,11–13]. Interestingly, the shape and size influences the optical and magnetic properties which can be tuned by using template like silica, activated carbon, surfactants etc. during growth process [14–16]. However, the usage of templates during crystal growth process introduces heterogeneous impurities and enhances the production cost [10]. Solvothermal/hydrothermal growth technique is a low cost templates free method for hematite crystallites with different size and shape by changing growth parameters. Different solvent combination has been used by the researchers for the growth of hematite crystallites with varying morphology [11]. Water-ethanol solvent combination promoted the growth of high coercive spherical shaped hematite crystals [11]. But, snow flake shaped hematite crystals were obtained when the growth is carried out with water as solvent of precursor salts [17]. Morphology of the hematite crystals were changed with ethanol-water combination ratio [18]. Grape and dumb bell structures were prepared by using ethanol and propanol as solvent of precursor salts [19]. These previous investigations indicate that the choice of solvent is an important factor for controlling size and shape of as grown crystals. Methanol is an organic solvent having relatively low viscosity but propanol is with higher viscosity. Further, shape and size control of hematite without templates is an interesting research problem, since it gives relatively impurity free crystallites. In the present work, we are reporting the template free solvo-hydrothermal growth of hematite and influence of viscosity of growth medium on morphology of the crystals and its optical and magnetic properties.

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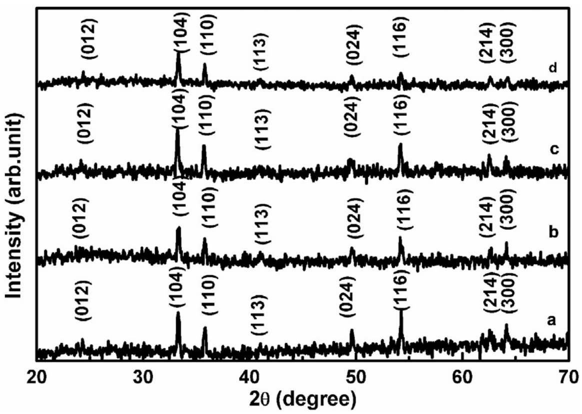

Fig. 1. XRD pattern of solvothermally grown hematite (α-Fe_2O_3) with different solvents (a) H-M, (b) H-MW, (c) H-P and (d) H-PW.

Table 1
Lattice parameters of solvothermally grown hematite (α-Fe_2O_3) with different solvents Methanol, methanol-water (1:1), propanol and propanol-water (1:1).

Sample	Lattice parameters calculated		Change in lattice parameters	
	a (Å)	c (Å)	Δa (Å)	Δc (Å)
Bulk JCPDS No. 33-0664	5.0356	13.7489	.	.
Methanol (H-M)	5.0486	13.7115	0.013	−0.037
Methanol-water (1:1) (H-MW)	5.0445	13.7052	0.009	−0.044
Propanol (H-P)	5.0473	13.7440	0.012	−0.005
Propanol-Water (1:1) (H-PW)	5.0396	13.7451	0.004	−0.004

2. Materials and methods

Hematite crystals were grown by solvothermal method using methanol (H-M), methanol-water 1:1 (H-MW), propanol (H-P) and propanol-water 1:1 (H-PW) solvents or solvent combination in each experiment. $FeCl_3 \cdot 6H_2O$ and NaOH salts were used as initial reactants in the molar ratio 1:3 [20]. The reactants were dissolved in corresponding solvents and taken in a Teflon beaker for the reaction process. The Teflon beaker containing precursor solution (50 ml) sealed inside an autoclave made of steel. The entire reaction set up was kept inside a furnace maintained at a temperature of 200 °C. After 8 h of reaction at 200 °C, system is allowed to cool to room temperature naturally. The experimental reaction product was taken out from the reaction system and filtered, washed and dried in air atmosphere. The pH of the precursor solution was measured as 2.90, 2.32, 1.47 and 2.76 for H-M, H-MW, H-P and H-PW respectively.

Structural characterisation of samples was done by X-ray diffractometer (XRD) (Rigaku D Max Diffractometer) with CuK_α radiation and Fourier transform infra-red spectrometer (FTIR) using IR Affinity-1-8400S by KBr pellet method. The morphology and elemental composition of the samples were examined using scanning electron microscope (SEM) (JEOL JSM - 6390LV) equipped with EDAX. Optical absorption of the samples was recorded with UV–visible (Jasco V-570) spectrometer, by dispersing sample in the ethanol medium and ethanol is taken as reference sample. Magnetic properties of the samples were measured using a vibrating sample magnetometer (VSM) attached to a physical property measurement system (PPMS, Quantum Design).

3. Results and discussion

3.1. Structural analysis

XRD patterns of samples grown with methanol, methanol-water, propanol and propanol-water match with JCPDS No. 33-0664 which corresponds to hexagonal hematite (Fig. 1) . EDAX analysis show the presence of iron and oxygen in all the samples which is in agreement with XRD data. Lattice parameter ‘a’ of samples under investigation are slightly increased (Δa) and its ‘c’ value slightly decreased (Δc) compared to bulk values (Table 1). The slight increase in dimensions of ‘a’ and slight reduction in dimension of ‘c’ is probably related to change in population of oxygen vacancies [21].

3.2. SEM analysis

SEM images of the samples are shown in Fig. 2 and inset shows crystalline size distribution histogram. Crystals grown with different solvents shows variation in crystalline size with respect to solvents used for the preparation. Spheroid shaped crystals are obtained from precursor solution made of methanol (H-M), methanol-water (H-MW) and propanol (H-P). Average size of spheroid crystals grown with methanol (H-M) medium is 0.749 μm and that of methanol-water combination (H-MW) and propanol (H-P) are 0.256 and 0.65 μm respectively. The pseudocubic crystallites with an average size of 1.281 μm are obtained when propanol-water (H-PW) combination is used for the growth process.

The pH and viscosity of the crystal growth media has considerable effects on morphology and size of crystals [18]. Hematite crystals grown with different solvents and solvent combination shows different morphologies as described previously. The lower pH of the solution generally encourages the growth of smaller crystallites [18] and higher viscous medium promote the growth of large sized particles. A combination of higher pH and viscosity of the growth medium is expected to fasten the aggregation process of smaller particles which leads to the growth of larger crystallites. The pH of the crystal growth mother solution made of methanol is 2.9 and the aspect ratio (average breadth/ average length) of crystals grown with this medium is about 1.21. But the addition of water in to methanol contributed to slight reduction of pH value to 2.3 and the aspect ratio of spheroid shaped sample obtained from this combination is 1.11. The pH of crystal growth mother solution made of propanol is 1.4 and the aspect ratio of crystallites obtained from this solution is 1.18. The pH of propanol-water combination is about 2.76 and this liquid is reported to have comparatively high viscosity with respect to other solvents used in the present investigation as growth medium [22,23]. Crystals grown with this combination of growth medium is having relatively higher aspect ratio as compared to other samples under study in the present work, probably originated due to the higher viscosity and relatively higher pH of the growth medium. These observations shows that, aspect ratio of the crystals grown with different solvents increases with increasing pH of the crystal growth mother solution [24]. The crystal structure (XRD pattern) of spheroid shaped samples grown with methanol, methanol-water and propanol solvents is identical to that of pseudocubic structured sample obtained with propanol-water solvent. Diffraction peak intensity corresponds to (1 1 6) plane of H-PW is found to be reduced with respect to other samples. This observation indicates that, initially formed spheroid shaped crystals undergo self-aggregation process in crystal growth medium (H-PW) for minimising the morphology dependant thermodynamic energy. This self-aggregation process of spheroid crystals will lead to the formation of more stable pseudocubic crystals with less thermodynamic energy. The variation of pH and viscosity of the solvent will affect the oriented