Study of the magnetic properties of Mn-doped iron titanate nanoparticles fabricated using natural mineral

1 | INTRODUCTION

Iron titanate is a wide bandgap semiconductor with an energy gap in the range of 2.58–2.9 eV [1–4] and has applications in various fields such as spintronics, photoelectrochemical, humidity sensing, gas-sensing, optoelectronics, and high-temperature integrated circuits [1–10]. Owing to its commercial and scientific interests, iron titanate (FT) has been considered as a potential candidate for applications, such as pigments [11], Li-ion battery anodes [12], non-linear optics [13], photocatalysis [14], UV fabrics [15], electrochemical energy storage [16], photodetector for electrolys of water [17–19], radiation-hardened electronics, microelectronics, and spintronics technologies, in numerous studies [20]. In recent years, there has been a growing interest in developing new materials based on magnetic as well as semiconductor materials for spintronics applications [5, 6, 19, 20], for which FT acts as a potential candidate.

In previous reports, FT nanoparticles and thin films were prepared by fabrication techniques such as solvothermal method [19], ball-milling, and hydrothermal processes [12, 21], sol–gel method [22], co-precipitation method [23], and ceramic method [24]. Talebi et al. [25] synthesised polycrystalline and spherical FT nanoparticles using wet chemical methods, and the prepared nanoparticles were paramagnetic in nature. Enhessari et al. [26] prepared polycrystalline, quasi-spherical, and paramagnetic–ferrimagnetic FT nanopowders via a solution-based approach. Guo et al. [27] fabricated amorphous FT nanotube arrays by anodization of the FeTi alloy, and their magnetic properties decreased as a result of disordered magnetic moments when the annealing temperature increased to 500 °C. Tang et al. [28] prepared FT composite particles using in situ hydrogen–thermal reduction method. The method used high-temperature treatment (650 °C), and the processing time was high (24 h) for fabricating crystalline nanoparticles. Further, the prepared composite particles were soft magnetic, and some of the iron metal particles were inlaid into titania, which led to superparamagnetic behaviour. Hessian and colleagues [29] synthesised ferrimagnetic pseudobrookite particles with unusual morphology of thin strings of joined particles using high temperatures starting from 900 °C. The synthesised material showed a weak ferromagnetic ordering and paramagnetic behaviour. Srinivas et al. [23] and Raghavender et al. [22] fabricated a soft ferromagnetic nanocrystalline FT through the co-precipitation technique and multistep process, respectively. Mahmoud and colleagues [30] prepared nanocrystalline pseudobrookite powder using inexpensive ilmenite ore obtained from the Abu Ghalaga region, Red Sea, Egypt. The synthesised FT had a weak magnetic system with ferromagnetic-paramagnetic behaviour. The preparation procedure involved a complicated process and required a high temperature treatment of 1000 °C.

Considering the issues such as complex process, multi-step approach, and high-temperature treatment, the present study aimed to prepare FT nanoparticles using a simplistic approach from an abundant natural source, ilmenite. Besides, the effect of Mn doping on the magnetic and semiconducting properties of FT was studied. The transition metal manganese (Mn) was chosen as a dopant material as the semiconducting property of these magnetic FT nanoparticles can be tuned by varying the concentration of the Mn dopant. The appearance of energy levels of Mn at different concentration narrows the band gap at different levels and enhances the magnetic as well as semiconducting property of the resultant materials. Such Mn-doped FTs have a significant impact on emerging technologies such as spintronics, magnetoelectronics, and rad-hard electronics [31].

2 | MATERIALS AND METHODS

Ilmenite sand used in this work was collected from coastal regions of Kanyakumari, Tamil Nadu, India. Polyvinyl alcohol (PVA, (C2H4O)n, MW: 86.09 g mol−1, 98% purity; Merck), manganese (II) nitrate hydrate (Mn(NO3)2·xH2O, MW: 178.95 g mol−1, 98% purity; Merck), sulphuric acid (H2SO4, 99.999% purity; Sigma-Aldrich) and all other solvents used were of analytical grade.

2.1 | Experimental procedures

First, the collected sand was subjected to a double-digestion process using concentrated sulphuric acid at 200 °C for 3 h in a muffle furnace. The weight ratio between the ilmenite sand and the concentrated sulphuric acid required for digestion process was 3:1. The resulting mixture was cooled to room temperature
and leached using double-distilled water to yield an iron titanium sulphate solution.

The prepared solution was stabilized with 1 wt% PVA relative to ilmenite sand, and the resultant solution was used as a precursor for the synthesis of iron titanate nanoparticles. The precursor solution was divided into two parts: the first part was taken as such, and the second part was doped with Mn with molar concentrations such as 0.2%, 0.8%, and 2%, using manganese (II) nitrate hydrate. Concentrated nitrate acid (HNO₃; 12 mol L⁻¹) was used to maintain the pH to 3 and was stirred continuously until the formation of the gel. Finally, the solutions were kept in a hot-air oven at 60 °C until the solution became dry, and it was triturated into powder using an agate mortar. The obtained dry gel was calcined at 500 °C for 6 h to obtain two variants of FT nanoparticles. The pure FT nanoparticles and 0.2%, 0.8%, and 2% Mn-doped FT nanoparticles were designated as FT, 0.2MFT, 0.8MFT, and 2MFT, respectively.

2.2 Characterization techniques

The chemical and phase compositions of the prepared samples were investigated using an energy-dispersive X-ray fluorescence spectrometer (EDXRF; EDX-720) and X-ray diffraction (XRD; X’Pert Pro), respectively. Crystallite sizes of the nanopowders were estimated in terms of Debye–Scherrer equation:

\[ D = \frac{0.9\lambda}{\beta \cos \theta} \]  

where \( D \) is the crystallite size, \( \lambda \) is the wavelength of the incident X-rays (in nm), \( \beta \) is the full width at half maximum (FWHM, in radians), \( \theta \) is the Bragg diffraction angle (in degrees). For further information regarding the elemental analysis, the elemental mappings were performed by the energy-dispersive X-ray spectroscopy (EDS).

The microstructure and morphology were analysed using scanning electron microscopy (SEM; JSM-6390LV; JEOL). Room temperature magnetization measurements were carried out using a vibrating sample magnetometer (VSM 7410; Lakeshore) in the field range of −20,000 to 20,000 Oe. The anisotropy constant (K in Oe) and the squareness ratio were calculated using the equations given below:

\[ K = H_c M_s / 0.98 \]  
\[ \text{Squareness ratio} = M_r / M_s \]

where \( H_c \) is the coercivity (in Oe), \( M_s \) is the saturation magnetization (in emu g⁻¹), and \( M_r \) is the remanent magnetization (in emu g⁻¹).

The electrical properties of the synthesised samples were measured using a four-probe resistivity meter (Keithley 6221) at room temperature in the delta mode operation. The powder samples of 0.7 g were made as disks of 13 mm diameter using a hydraulic pellet-maker by pressing at 115 kg cm⁻². The source current (−20 to 20 μA) and measurable voltage (1 V) were always maintained for conductivity measurements of the sample. The input power was supplied at a frequency of 1000 Hz.

The average resistance values were measured using the following equation:

\[ \rho = R (A / l) \]  

where \( R \) is the resistance value (in Ω) obtained from the four-probe measurement, \( \rho \) is the resistivity (in Ω-cm), \( l \) is the width (0.3 cm) of the pellet (in cm), and \( A \) is the cross-sectional area (1.3 cm²) of the pellet (in cm²).

3 RESULTS AND DISCUSSIONS

3.1 Structural studies: XRD pattern

The structural and phase purity of FT and MFT nanoparticles were analysed using XRD patterns, as shown in Figure 1. The clear diffraction peaks showed that the synthesised nanoparticles are crystalline in nature. The diffraction peaks
corresponding to (012), (104), (110), (113), (024), and (116) reflections matched well with the rhombohedral structure of FT according to JCPDS file no. 75-1211 [23]. No peaks related to Mn dopant and no trace of impurity phase such as manganese oxide are detected from the XRD patterns, suggesting significant incorporation of Mn ions in the FT samples. However, there is a systematic shift in the (104) peak position toward lower “d” values with increasing Mn concentration, and the blue shift of the high-intensity peak is seen in the magnified image shown in Figure 1(b). This implies that Mn atoms effectively occupy Fe/Ti sites without changing the rhombohedral structure. Using Debye–Scherrer equation, pure FT was calculated, whose average crystallite size was 56 nm, and on increasing the concentration of Mn from 0.2%, 0.8% to 2%, the average crystallite size decreased to 41, 36, and 29 nm, respectively. The reduction in crystallite size is due to the lattice distortion caused by the radius difference between dopant atoms and the replaced elements [32].

### 3.2 Microstructural studies and elemental analysis

Figure 2 represents the microstructural characteristics of the natural mineral ilmenite sand. From the selected zone of SEM and the corresponding EDS spectrum, it can be clearly seen that the composition of the ilmenite sand contains Fe, Si, Ca, Ti, and O.

The surface morphology of the prepared samples is shown in Figure 3(a–d). In FT and 0.2MFT, the nanostructures are homogeneously distributed, and the presence of both irregular and nano spherical morphologies are observed. In addition, the nanostructures are closely packed compared to Mn-doped samples. It is also observed that 0.8MFT and 2MFT have nano spherical morphology with dimensions less than 200 nm, and the voids between the nanostructures increase with Mn concentration.

The chemical composition of the prepared samples was investigated using energy-dispersive X-ray analysis, and the results are shown in Figure 3. The EDS data analysis identifies the presence of Fe, Ti, O and Mn elements in the doped samples and except Mn in the FT sample, implying that Mn was successfully incorporated in the structure of FT. For further confirmation, elemental mappings were performed for 0.8MFT sample and the findings are displayed in the Figure 4. It is demonstrated that the successful doping of Mn and even distribution of Fe, Ti, O and Mn elements in 0.8MFT sample.

### 3.3 Magnetization studies

The magnetic properties of FT and MFT were analysed using typical hysteresis curves, as shown in Figure 5 and the corresponding magnetic parameters are listed in Table 1. A similar trend was observed in our work also. In general, the magnetic moments of ferrimagnetic materials have non-zero magnitude and are antiparallel in nature. When sum of the magnetic moments of the atoms is equal, spontaneous magnetization disappears. When the magnetic moments of the atoms are not equal and have large differences in magnitude, induced magnetization occurs [33-35]. In this study, the atoms in the synthesised materials were Mn, Fe, Ti, and O. It is predicted that the magnetic moments of the atoms in FT are not equal, and thus spontaneous magnetization occurs. The saturation magnetization values of FT and MFT decreased from 2.2 to 1.4 emu g–1 after introducing the dopant atoms. Such decreases in Ms after Mn doping are attributed to factors such as stoichiometry of the cations and random particle size distribution [36]. The Ms values of the prepared samples vary similar to those of Mr. According to Neel’s theory [37], the magnetization is denoted by $M = |M_B - M_A|$, where $M_A$ and $M_B$ are magnetic moments of A- and B-sites, respectively. The cationic distribution among A- and B-sites depends on the preparation conditions and particle size [11]. The magnetic moment values of the cations (Mn$^{2+}$, Fe$^{3+}$, and Ti$^{3+}$ ions) based on the number of unpaired electrons were 5, 5, and 2 µB, respectively [38]. Any change in the magnetic moments of the cations exerts a profound effect on the magnetization values. Hence, after doping Mn in FT, it will preferentially occupy B-site, which may result in the reduction of the magnetic moment of B-site [39]. This could be a possible reason for the reduced Ms values obtained after doping Mn. However, the coercivity value of MFT varied between 557 and 707 emu g–1, which are more significant than FT, whose value was 387 emu g–1. Meng et al. [40] explained that the $H_c$ values of ferrites are dependent on the microstructural properties such as particle size, strain, defects, vacancies, dislocations, and structural properties such as the distribution of cations in the interstitials. The highest Mr value of 1.468 emu g–1

| TABLE 1 Magnetic parameters of FT and various concentrations of Mn-doped FT samples |
|-----------------|----------|----------|----------|----------|
| Magnetic properties | FT  | 0.2MFT  | 0.8MFT  | 2MFT  |
| Saturation magnetization (Ms) (emu g–1) | 2.285 | 1.427 | 1.468 | 1.41 |
| Remanent magnetization (Mr) (emu g–1) | 0.979 | 0.26 | 0.302 | 0.24 |
| Coercivity (Hc) (Oe) | 386.56 | 652.17 | 557.8 | 707.52 |
| Squareness ratio (Mr/ Ms) | 0.428 | 0.185 | 0.206 | 1.702 |
| Anisotropy constant (K) (Oe) | 903.29 | 951.6 | 835.6 | 1017.2 |
was observed for 0.8MFT. Further increasing the concentration to 2% in MFT, saturation value found to decrease. This behaviour is explained as follows: at lower Mn concentrations, the magnetization originates from isolated Mn$^{2+}$ ions. With an increase in dopant concentration, the average distance between Mn$^{2+}$ ions decreases, resulting in the pairing of nearest dopant ions and a reduction of $M_s$ value [41]. It is commonly noticed that the $H_c$ value of the ferrites decreases with an increase in the overall grain size due to the pinning of the domains by grain boundaries. Larger grain size has a smaller grain boundary area, which leads to less pinning [42, 43].

The increase in the $H_c$ value of the MFT might be caused by improved crystalline behaviour and well-defined nanosphere-like morphology. It can be concluded that MFT samples are hard ferrimagnetic material characterized by coercivity values greater than 100 G [44]. The squareness ratio and $K$ values increased on increasing the Mn content, owing to the addition of magnetic Mn$^{2+}$ ions, which significantly influences the magnetic moment interactions [45]. If the squareness ratio value is more significant than 0.5, it indicates that the sample consists of single magnetic domains; otherwise, it has multi magnetic domains [46]. The fabricated samples such as FT, 0.2MFT, and 0.8MFT showed the squareness ratio values below 0.5, which typically comprise multidomain magnetic grains. However, the sample 2MFT showed single-domain magnetic grains in the structure. The MFT ferrimagnetic nanoparticles had high coercivity values, which makes them a suitable candidature for applications such as magnetic recording, memory devices, spintronics, and sensors.

### 3.4 Electrical resistivity studies

Though the investigations on various properties of iron titanate have been made earlier, but electrical properties concerning doping on iron titanate nanoparticles synthesised from
natural source ilmenite have not been reported. An essential aspect of optimizing the properties of the transition metal elements/compounds is an understanding of the nature and quantity of the dopant. It has been observed that the concentration of Mn strongly influences the electrical properties of Mn-doped metal oxide nanostructures. In some instances, an increase in Mn concentration resulted in an increase of resistivity and a decrease of magnetization [47].

In the present work, the semiconducting properties such as resistance and resistivity of the fabricated FT and MFT nanoparticles, determined using four-probe method, are shown in Table 2. The pristine iron titanate nanopowders without an addition of the dopant Mn demonstrated higher resistance and resistivity values comparing to the MFT samples. This implicated that the as-fabricated pristine nanopowders were devoid of carrier concentration. Adding a low concentration of Mn in the pristine samples, the resistivity of the 0.2MFT sample decreased by nine-fold, thereby improving the electrical conductivity. It is presumed that the addition of Mn ions contributed additional electrons to the conduction band. Thus incorporation of Mn in FT significantly decreased the resistivity values.

It can also be observed that the resistance and resistivity values increased with an increase in the dopant concentration, even though the values are lower than the pristine FT sample. The reason for this behaviour is ascribed to the incorporation of Mn$^{2+}$ ions resulting in hole doping, which aids in the recombination of electrons in the sample, thus reducing the carrier concentration. This decrease in the carrier concentration resulted in an increase in resistivity, on increasing the concentration of Mn doping [48]. These results are also supported by XRD results. It can be explained by the fact that the decrease of crystallite size increased the total grain boundary fraction, which in turn enhances the grain boundary scattering, thus, results in an increase of electrical resistivity [49]. Eventhough doping of Mn$^{2+}$ ions is highly desirable for improving the magnetic properties, which in turn it increase the resistivity values.

### 4 | CONCLUSION

A cost-effective methodology has been proposed for the large-scale production of FT nanoparticles using a natural source, ilmenite. It was found that doping with the transition metal manganese exerts a considerable effect on the structural, magnetic, and electrical properties on FT nanoparticles. The crystallite size decreased gradually on increasing the Mn content, due to lattice distortion caused by Mn and FT atoms. This work demonstrated that an ionic radius of Mn favours grain growth, which is necessary to achieve ferrimagnetic property. With an increase in the dopant concentration, $M_\chi$ value decreased, which is attributed to the pairing of the nearest dopant ions. Though the addition of Mn was responsible for higher magnetic moments, it essentially reduced the carrier concentration and increased the resistivity values. Thus, a combination of magnetic and semiconducting properties of MFT could be used in applications such as spintronics, semiconductor device, magnetic recording, memory devices, and sensors.

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