ISSN (Print) 1226-1750
ISSN (Online) 2233-6656
Journal of Magnetics 24(3), 367-370 (2019) https://doi.org/10.4283/JMAG.2019.24.3.367

Modified Beach Placer Ilmenite: Dilute Magnetic Oxide

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(Received 5 September 2018, Received in final form 11 September 2019, Accepted 16 September 2019)

Naturally-occurring Ilmenite ore is usually a mixture of Ilmenite ($FeTiO_3$) and hematite (Fe_2O_3). Synthesized solid solutions of Ilmenite and hematite are known to have interesting magnetic and electric properties. In the present study, we report that naturally occurring Ilmenite sintered with titanium dioxide also has low electrical resistivity and can be a natural resource for applications as electronic materials as envisaged for the system Ilmenite-hematite.

Keywords : Solid Solution, pseudo-brokite, resistivity, magentization, semi-conductor

1. Introduction

In recent years dilute magnetic oxide based on ZnO and TiO_2 are being studied due to their potential application as semiconductor-based spintronic devices. The most common use of spintronics today is in computer hard drives. Naturally occurring beach placer Ilmenites are rich Fe-titanates and have been known to geologists and geophysicists for a very long time. They exist primarily as three minerals, namely, Ilmenite ($FeTiO_3$), pseudo-brokite ($FeTi_2O_5$) and ulvospinel ($FeTiO_3$). Thus Ilmenite $FeTiO_3$ is a naturally occurring mineral present in ingenious rocks derived from the upper mantle. Ilmenite is an economically important mineral primarily because of its role in the production of titania pigments and the metal titanium. Ilmenite is also the most prominent radiation shielding material and is extensively used for shielding buildings and other facilities from dangerous radiation leakage in the vicinity of nuclear reactors. It is one of the mixed-valence transition metal-bearing minerals, in which Fe can be in two different oxidation states, Fe^{2+} and Fe^{3+}. Similarly, Ti can be in Ti^{3+} and Ti^{4+} states. Its magnetic properties coupled with the semiconducting nature are also of importance.

A previous study on synthetically prepared solid solutions of Ilmenite-Hematite shows that they have interesting magnetic and electric properties [1]. Similarly, studies on the solid solution powders of Ilmenite-Hematite prepared by chemical co-precipitation exhibited ferromagnetism [2]. Natural Ilmenite does contain a significant amount of Hematite (Fe_2O_3) as observed previously [3, 4]. Thus Natural Ilmenite is therefore essentially a solid-solution of Ilmenite ($FeTiO_3$) and Hematite (Fe_2O_3). In the present study, we have chosen Ilmenite mined from beach placer minerals. It was further beneficiated and enriched. The motivation for the present study is to understand the magnetic nature of natural Ilmenite. Hence, in the present paper, a magnetic characterization along with an electrical resistivity study of Ilmenite is presented.

2. Experimental

2.1. Sample preparation

For the present study Ilmenite in the pure and beneficiated form is the starting material. X-ray diffraction study was carried out on the samples ground to a mesh of 150 using a SIEMENS -D500 X-ray diffractometer with the angle varying from 20 to 90° of 2θ. The conventional wet chemical analysis was carried out on the ground sample. The samples were prepared by sizing the ore to 150 mesh. Ceramic samples were prepared using standard techniques. Appropriate molar weights of each; ground Ilmenite, Titanium dioxide, and carbon oxides were weighed and mixed thoroughly in agate mortar along with a small amount of acetone to homogenize the mixture. This mixture was taken in an alumina crucible and calcination was carried out at 1000 °C for 2 hours. The furnace was a graphite crucible furnace and a steady flow

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of argon (IOLAR – 1) was maintained during the entire process of heating and cooling. After allowing the sample to cool down to ambient temperature overnight, it was removed and ground well again in an agate mortar with a small amount of acetone. Then, the material was compacted at an applied pressure of 10 ton into green pellets of 25 mm diameter and about 2-3 mm thickness. These pellets were then sintered in the same graphite furnace under a flowing argon atmosphere at 1100 °C temperatures. Small pieces of size 2 mm × 2 mm × 4 mm were cut from the sintered pellets and used for characterizations.

2.2. X-ray Diffraction

X-ray diffraction was again carried out on the sintered samples to understand the resistivity behavior. Small pieces of size 2 mm × 2 mm × 4 mm were cut from the sintered pellets and used. The instrument used was the SIEMENS -D500 X-ray diffractometer with the angle varying from 20 to 90° of 2θ.

2.3. Vibrating sample magnetometer studies

Vibrating Sample Magnetometer (VSM) was used to measure the magnetic hysteresis curve (also known M-H curve) for which a set of samples were prepared. For the magnetic characterization using a VSM, the sample geometry needed is machined as per the size of the sample holder. Samples were cut using slow speed diamond wheel cutter to the desired dimension of 3 mm × 3 mm × 1 mm from the sintered samples as above.

2.4. Resistivity measurements

Small pieces of size 2 mm × 2 mm × 4 mm were cut from the sintered pellets and used for resistivity measurements. For the resistivity measurements, four contacts to the sample were made using a two-part silver epoxy. Vander Pauw's four-point method was used to measure the electrical resistivity. The apparatus used for this measurement consisted of a Keithley constant current source (model 6221) and a Keithley nanovoltmeter (model 2182 A).

For the room temperature resistivity, two wires were used to pass a constant current and the voltage drop across the remaining two wires was measured. After an accurate measurement of the distance between the voltage leads, the resistivity (r) of the sample was evaluated using the formula.

$$\rho = RA/L,$$

where R is the resistance (R = voltage drop/constant current passed) as measured above, L is the distance between the voltage leads and A is the cross-sectional area of the sample under test. Scanning electron microscopy was carried out on the mounted and polished samples.

Low-temperature resistivity study was carried out from ambient temperature to the lowest possible (around 20 K) using a closed cycle refrigerator. The resistivity data were taken for both the cycles i.e. while cooling and heating it back to the ambient temperature.

3. Results and Discussion

3.1. X-ray Diffraction

The X-ray diffraction data of Ilmenite is shown in the figure below:

The X-ray data show the mineral Ilmenite is rich in Ti along with Fe in its different oxidation states. This confirms that the fact that the starting materials did not have any major impurities as revealed by the X-ray data.

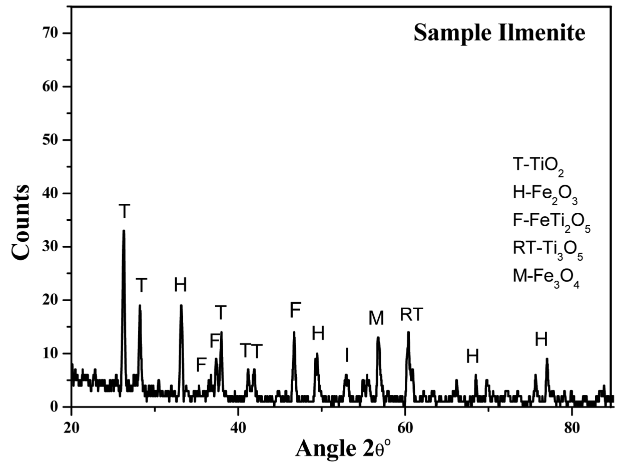

Fig. 1. X-ray diffraction plot of Ilmenite.

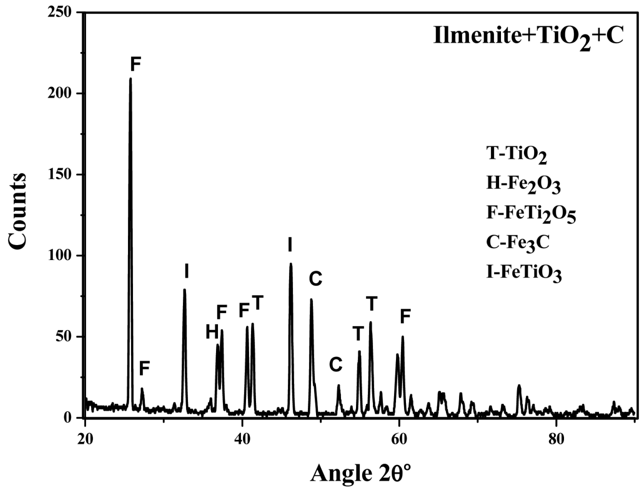

Fig. 2. X-ray plot of a solid solution of Ilmenite, Titanium oxide, and Carbon.

3.2. X-ray Diffraction of the solid solution samples

Figure 2 shows the X-ray plots of the solid solution sample. It is seen that the solid solution had some possibly untreated Ilmenite, Titanium dioxide in addition to new phases like $FeTi_2O_5$. There was no trace of any untreated carbon on the other hand formation of cementite (Fe_3C) has been observed. A number of studies have been reported in the literature on the phase transformation occurring during the oxidation and reduction of Ilmenite ores [5]. An analogous phase transformation occurring during the reduction process was observed. The authors note that Pseudobrookite was a prominent phase formed during the reduction process.

Various experimental investigations discussed in the literature show that Pseudobrookite is a product of reduction of Ilmenite ore under various conditions of reduction. Hence, Pseudobrookite is always present as a product of the reaction in all the experiments. It is also reported that the Ti_3O_5 which is an end-member of the $FeTi_2O_5$-Fe_2TiO_5 solid solution series is a good conductor of electricity [6].

3.3. Resistivity measurements

The resistivity results for the Ilmenite and the solid solution samples of Ilmenite, Titanium oxide and Carbon sintered under identical conditions are given in Table-1

Thus from Table 1 above it is seen that the present solid solution of Ilmenite, titanium dioxide and carbon also showed a very low room temperature resistivity which is of a few ohm-cm, compared to Ilmenite which of the order of few kilos ohm-cm. Herein also a similar non-stoichiometric oxide in the form of $FeTi_2O_5$ is believed to show a similar behavior in the resistivity (inverse of conductivity).

Further, as observed by the X-ray diffraction (Fig. 2) the transition between Ti^{4+} and Ti^{3+} would significantly contribute to an enhanced electrical conductivity. Therefore, the samples sintered under reducing conditions always show a lower resistivity. Pseudobrookite is known to be a solid solution of ferrous ($FeTi_2O_5$) and ferric (Fe_2TiO_5) Pseudobrookite. Variation in the relative proportion of the two components of solution can alter the electrical resistivity. This explains the variation in the electrical resistivity observed in different experiments through the phases detected by XRD is similar. It may be noted that XRD cannot resolve the relative proportion of ferrous and ferric Pseudobrookite in the solid solution. The influence of sintering temperature on the resistivity is not clear.

Table 1. Resistivity values of the sintered samples.

S. No	Sample chemistry	Sintering Condition	Resistivity Ω-cm
1	Ilmenite	1. Pre-fire at 1000 °C/2 h 2. Sinter at 1100 °C/3 h	52.88 K
2	$0.7FeTiO_3+0.20TiO_2$ $+0.10C$	1. Pre-fire at 1000 °C/2 h 2. Sinter at 1100 °C/3 h	13.24

3.4. Low-temperature Resistivity measurements

Fig. 3 below shows the low-temperature electrical resistivity study carried on the solid solution of Ilmenite with Titanium dioxide and Carbon

Measuring the temperature dependence of resistivity reveals some important differences between metals, insulators, and semiconductors. There are a variety of factors that influence resistivity (and thus its inverse, conductivity), and identifying these mechanisms and fitting the experimental data can reveal properties of the material, such as the band gap energy, or the temperature coefficient of resistance. There are two important factors that contribute to the conductivity of a material: the availability of free electrons and the ability of these electrons to move freely through a material. At high-temperature mobility of ions (holes) may also contribute towards enhancing conductivity in ceramic materials. For a conducting metal with free valence electrons, the factor limiting conductivity is the lattice vibrations which scatter moving electrons; as temperature decreases, these vibrations (and thus the resistivity) also decrease. In an insulator, the electrons are unable to break free from the filled valence band, so there is little conduction. For a semiconductor, the energy gap (about 2.5 e.v.) is small enough that there are some free electrons at higher temperatures. Since the factor limiting conductivity for a semiconductor is the availability of free electrons, resistance

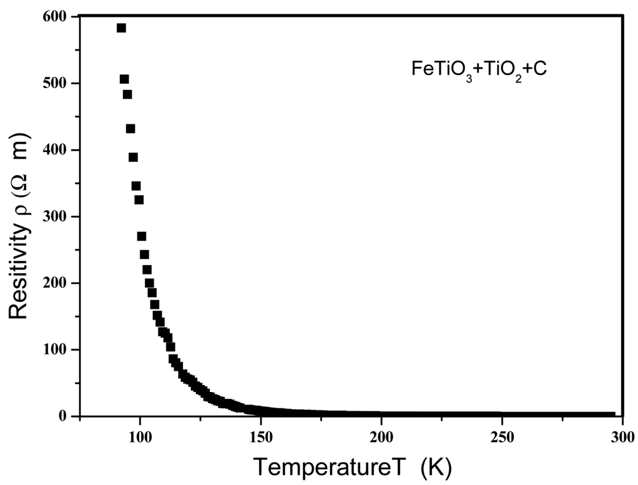

Fig. 3. Low-temperature Resistivity study of a solid solution of Ilmenite with Titanium dioxide and Carbon.

increases with decreasing temperature, which is the reverse of the behavior observed in a metal. Thus from the discussion, it is clear that the low-temperature resistivity data as observed herein suggest the semiconducting behavior of the solid solution samples. This confirms the semiconducting behavior of the samples under study.

3.5. The magnetization of the solid solution sample

To further understand the magnetic behavior of the solid solution samples, a room temperature Vibrating sample magnetic study was carried out. Table 2 below gives the values of the different magnetic parameters obtained. It can be seen that the solid solution shows a good magnetic behavior also in addition to being a semiconductor. This is in contrast to earlier studies (1) wherein it is observed that natural Ilmenite in solid solution with hematite shows interesting electrical and magnetic properties.

The observed magnetic and semiconducting behavior finds an explanation in the fact that the metastable phase identified in the x-ray data of the solid solution sample as $FeTi_2O_5$ is responsible. This adds one more member to the family of Iron-titanates, Fe-Ti-oxides, with their unique electrical, dielectric and magnetic properties that can be exploited for potential applications in microelectronics, rad-hard electronics, and spintronics. Further, in this study, it is also noted that the addition of carbon as a reducing agent changes the reaction kinetics. The above results suggest that in the reduction of Ilmenite ore at temperatures of 1000 °C, the energy provided is inadequate to bring about the appreciable reduction of Fe^{2+}. However, a significant reduction occurs at temperatures above 1000 °C, which is in agreement with the earlier workers [6, 7] Comparing with the study of [8, 9], the reduction degree of the Ilmenite is lower because of the high content of impurities including manganese, silica and silicon oxides, and a small quantity of magnesium oxide. Table 2 gives the magnetization data of Ilmenite along with the solid solution of Ilmenite, titanium dioxide, and carbon. From the Figure 4 which is the hysteresis loop (M-H curve) of both Ilmenite and the solid solution, it is clear that from the present study a solid solution of Ilmenite, titanium dioxide and carbon has the necessary electrical conductivity and ferromagnetic characteristics.

Table 2. Magnetization data of Ilmenite ore and the solid solution.

Sample	Coercivity (Hc Gauss)	Magnetization (Ms emu/g)	Retentivity (Mr emu/g)
Ilmenite	27.063	0.48737	1.2068×10^{-3}
Ilmenite+TiO_2+C	16.624	9.5729	38.145×10^{-3}

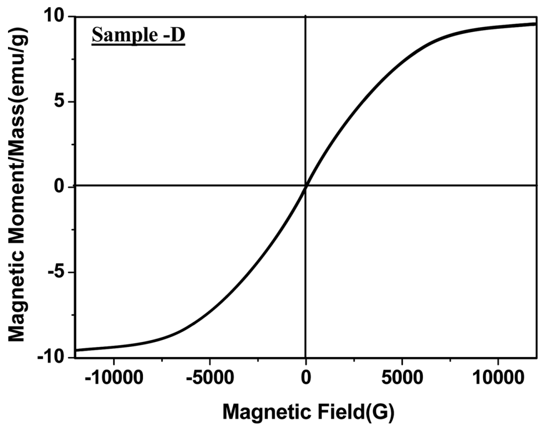

Fig. 4. Magnetization versus applied field plot of a solid solution of Ilmenite, Titanium oxide, and Carbon.

4. Conclusions

The Beach placer Ilmenite has been studied for its electrical and magnetic properties. The present work shows beach placer Ilmenite in its form has a very high resistivity, however, following a reduction with carbon and Titanium oxide brings down its resistivity and is seen to exhibit a semiconducting behavior. In addition, it is also shown that this solid solution of Titanium dioxide and carbon has a typical magnetic behavior as seen from the magnetization data. The possibility of this solid solution as a candidate material for magnetic semiconducting application is evident which could be cost effective too. One possible application is for use in the manufacture of varistors which needs to be explored.

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