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Material Science Properties of Nano-Ilmenite - A Review

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Abstract: Ilmenite is one of the predominant beach placer mineral. The ilmenites can also be called as natural ferrites and it is the chief ore of titanium dioxide. The ferrites are prepared using ceramic technology. The synthesis parameters also play a key role in governing ferrite properties. The important electric and magnetic properties of ilmenites make them suitable for various applications. Apart from their applications there are many drawbacks in using ceramic technology. The manipulation of ilmenite in an atomic, molecular and super molecular scale gives rise to nano-ilmenites. Nano-ilmenites are synthesized by various methods. The methods involved are ball milling and sol-gel method. These nano particles have wide range of applications irrespective of fields. In India most of the ilmenite deposits are along the East Coast and are concentrated in the states of Tamil Nadu, Andhra Pradesh and Odisha. The characterization of the ilmenite particles is done by optical microscopy, XRD and electron probe microanalysis (EPMA). These Ilmenites are applicable to material sciences. Synthesized nano-ilmenites from these East Coast Ilmenites show some special properties and their possible applications as nano materials are also illustrated.

Keywords: Nano-ilmenites, Synthesis, Ball milling, Sol-gel, East Coast Ilmenites.

I. INTRODUCTION

Ilmenite is a common accessory mineral found mostly in igneous rocks. It is black iron titanium oxide with composition FeTiO_3 . It is used mostly in the manufacturing of titanium dioxide (TiO_2), pigment, whiting, polishing and abrasive. Mostly ilmenites are formed during slow cooling of magma chambers and is concentrated through process of magmatic segregation. As the magma cools crystals of ilmenite form at particular temperature and these crystals are heavier than surrounding melt and sink to bottom of magma chamber. This results in the accumulation of ilmenite and similar minerals like magnetite are also present at the bottom of magma chamber. The ilmenite bearing rocks are often gabbro, norite or anorthosite. It also crystallizes in veins and cavities and sometimes occur as well formed crystals in pegmatite. Ilmenite have high resistance to weathering. When rocks containing ilmenite weather, grains of ilmenite disperse with sediment. Grains with high specific gravity segregate during stream, transport and accumulate as heavy mineral sands. Ilmenites are primary ore of titanium metal. It is used in manufacture of automobile tools. Ilmenites are mostly present as beach placers in Kerala, Tamil Nadu, Andhra Pradesh, Odisha, Gujarat, and Maharashtra and east coast ilmenite is shown in Fig.1.

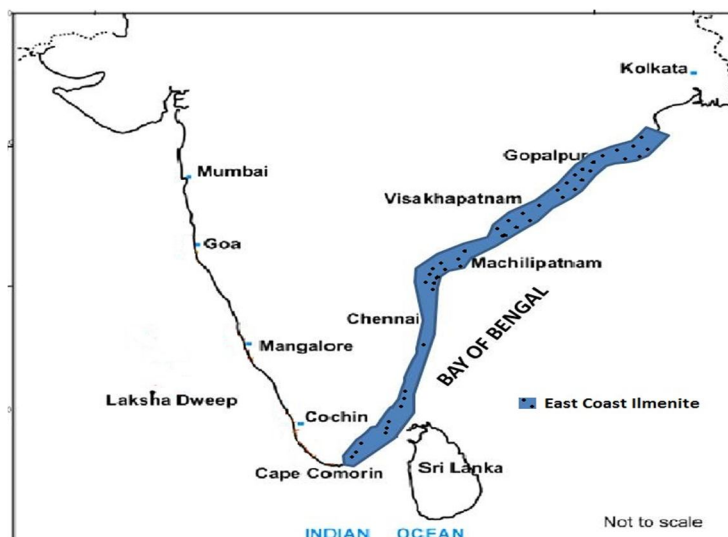


Fig. 1. Map showing occurrence of Ilmenites along East Coast of India.

II. ILMENITES AS NATURAL FERRITES

Ferrites are the important class of ceramic magnetic oxides materials which show the property of electric insulator and magnetic conductor. Ferrites are of two types namely soft ferrites and hard ferrites based on their properties. The important electrical and magnetic properties of ferrites are high electrical resistivity, low eddy current, dielectric losses, high saturation magnetization, high permeability etc. These properties makes ferrites useful in various applications like transformer core, antenna etc. Because of their low eddy current and dielectric losses they are used in various applications like switch mode power supplier transformers, inductors etc. Usually ferrites are prepared by ceramic technology, using high purity metal oxides, it has many drawbacks in it. With the advent of nano technology ferrites have been prepared in nano size using different chemical methods. The properties of these nano sized ferrites are found to be very interesting and superior to that of their bulk counterpart. Synthesis parameters like pH, fuel, annealing temperature play an important role in governing the properties of nano ferrites. Nano technology is the manipulation of matter on an atomic, molecular and super molecular scale. Nano technology refers to particular technological goal of manipulating atoms and molecules for fabrication of macro scale products. It can be defined as manipulation of matter with at least one dimension sized for 1 to 100 nanometers. Nano crystals (NCs) or nano particles (NPs) are the fundamental building blocks in nano science with high surface to volume ratio, different physical and chemical properties from their bulk materials (Hades et al). The unique properties of nano particles are being utilized in the applications like optoelectronics, energy conversion, magnetic storage or nano medicine. Ilmenite is an abundant material in Earth crust which is anti ferromagnetic, insulator, absorbing material and semiconductor (Tang Xing et al). It can be used in many applications like radar absorbing material, chemical catalyst, optoelectronics and emulsions etc. (Leion et al). It is a basic raw material for the production of TiO_2 , Ti and as chemical catalyst oxygen carrier for solid fuels. India has large resources of heavy minerals which occur along coastal area and in inland placers. There are seven minerals in these beach placers. They are namely ilmenite, Leucoxene (Brown ilmenite), sillimanite, rutile, zircon, garnet, sillimanite and monazite. Leucoxene is an alteration product of Ilmenite and found associated with Ilmenite. Ilmenite and rutile are the chief sources of titanium. Various ilmenite deposits along the East Coast are listed below.

III.ILMENITES OF EAST COAST OF INDIA

Ilmenite, an abundant ore mineral of titanium occurs in India along the coastal beach sands of Tamil Nadu, Andhra Pradesh and Odisha. Various works have been carried out by Researchs from dominant deposits of East Coast of India in order to determine the chemistry and ore mineralogical properties. Various deposits along the East Coast are listed in Table.1.

TABLE I. Ilmenites of East Coast of India. (Source: Department of Atomic Energy, Mumbai)

Tamil Nadu	Ilmenite Reserves (In million tones)
1. Kudiraimozhi	22.86
2. Ovari-Periyatalai-Manapadu (Teri)	24.01
3. Sattankulam Teris	41.26
4. Cuddalore-Pudupattuchavadi	4.67
5. Vayakallur (Block I-IV)	3.54
6. Manavalakurichi	2.04
7. Midalam	1.64
Andhra Pradesh	
1. Bhavanapadu Hukumpet	10.18
2. Kakinada (Phase I-VIII)	13.84
3. Kalingapatnam	5.80
4. Narasapur	2.92
5. Nizampatnam	19.26
6. Srikurmam(South)	8.6
7. Visakhapatnam (Bhimunipatnam)	2.88
8. Amalapuram (Phase I-III)	3.1
9. Pandurangapuram-Voderevu	10.39
10. Vetapalem Coast (Chirala coast)	5.31
Odisha	
1. Brahmagiri (Phase IV)	37.98
2. Chatrapur	26.72
3. Gopalpur (Phase I-IV)	6.39

IV. ILMENITES OF TAMILNADU

Tamil Nadu is one of the states along the East coast of India in which the ilmenite deposit extended over a length of 6 km with an average width of 44 mts.

A. Manavalakurichi

In the state of Tamil Nadu, among various placer deposits Manavalakurichi placer deposit is one of the predominant one. Based on the previous studies carried out in this particular deposit it was concluded that the average depth of the deposit was 7.5mts, the total heavy mineral content of the deposit was 39%. Ilmenite is predominant mineral with a grade of 24% in raw sand, 8% rutile, 0.9% leucoxene, 2% zircon and 1% monazite, 3.5% sillimanite and 5.5% garnet (Ali et al). The earlier studies done in this particular Manavalakurichi deposit shows good stoichiometry of TiO_2 (59.193% to 54.151%) and FeO (42.034 % to 45.885%). Magnesium (0.025% to 2.015%) and Manganese (0.096% to 0.902%). The TiO_2 content of ilmenite is higher or lower than the ideal value (52.65%) (Rao et al).

B. Ilmenites of Navaladi and Surugudi area of Teri

This is the another important deposit in the Teri of Tamil Nadu. Placers of Navaladi and Teri indicate 33.22% and 35.70% of magnetic minerals and 34.20% and 37.26% heavies respectively. Navaladi samples contain higher amounts of garnet and good amounts of ilmenites while Teri sample contain higher amount of ilmenite and minor amounts of rutile.

V. ILMENITES OF ANDHRA PRADESH

In the state of Andhra Pradesh ilmenite deposits occur in the areas of Visakhapatnam-Bhimunipatnam, Kalingapatnam, Srikurmam, Narsapur Kakinada etc.

A. Visakhapatnam-Bhimunipatnam

The Visakhapatnam-Bhimunipatnam is in the state of Andhra Pradesh is one of the promising deposits. The demand for ilmenite and its value added products has been increasing these days. India has a total reserves of about 278 million tons (Mukherjee et al) of which Andhra Pradesh alone holds about 103.05 million tons (Ravi et al).

Based on the previous available literature it was concluded that in the beach samples the TiO_2 content varies from 47.36% and iron content of the deposit is 47.38% (Jagannadha Rao et al). Thus it can be concluded that the ilmenite of this deposit has higher total iron and lower TiO_2 contents when compared to the compositions of ilmenite's from other area.

B. Srikurmam

Ilmenite deposits along Srikurmam coast in Andhra Pradesh is one of the richest beach placer deposits along the East coast of India. This deposit has an average grade of 34% Total Heavy Mineral (THM) concentration with abundant ilmenite and garnets. The TiO_2 content of this particular deposit varies from 50.04% to 52.05% and the range of iron varies from 45.41% to 47.53% (Jagannadha Rao et al).

VI. ILMENITES OF ODISHA

A. Chhatrapur

Chhatrapur is an area which is 150 km from Bhubaneswar which is in the state of Odisha. Chhatrapur deposit is along the coast of about 18 km long and a width of about 1.5 km is one of the largest deposits in India. This deposit is at a height of 1 to 15 km from the surface of water table and is spreaded over an area of 24.64 km^2 (Siba). Ilmenite has 50% TiO_2 (Siba) content is associated with the minerals like garnet, zircon, rutile, sillimanite etc. Chhatrapur deposit is generally in the form of sand dunes. The heavy minerals are concentrated at the surface and as the depth increases, the concentration decreases. The methodology which is used to produce the ilmenite in this particular area has three steps to carry out. They are namely mining or dredging, heavy mineral up gradation and mineral separation.

B. Brahmagiri

Various studies have been carried out on Brahmagiri placer deposits of Puri district of Odisha. This deposit contains potential amount of heavy minerals whose content is about 29%.

VII. METHODOLOGY

The nano-ilmenites are synthesized by reducing the size of the sample into required nano particles. There are various methods to synthesize nano ilmenites. The different types of methods are described below.

A. Ball Milling

Ball milling is a method of synthesizing nano-ilmenites. The ilmenite particles are brought to nano size by top-down approach. 25gms of ilmenite (9.8 μ m) were placed in 80ml tungsten carbide mixing jar along with 5 tungsten carbide milling balls. One tungsten carbide milling ball yields one ball to powder weight ratio of 10:1. The particles underwent the process of milling at 400 rpm for 48 hrs. To prevent the powder from sticking to balls and walls of the jar, methanol was added to it. Once the methanol gets evaporated, the powder is taken out of the jar and collected in a vacuum container.

B. Sol-gel Method

Sol gel auto ignition is a method of synthesizing nano-ilmenites. The A.R grade citric acid ($C_6H_8O_7 \cdot H_2O$), titanium dioxide (TiO_2) from Sigma-Aldrich, ferric (III) nitrate non-anhydrate ($Fe(NO_3)_3 \cdot 9H_2O$), were used as precursor materials. By dissolving nitric acid with titanium dioxide, titanium nitrate was prepared. To obtain a clear solution ferric nitrate and citric acid are dissolved in de-ionized water. These two solutions are mixed for 30 minutes to get uniform mixture solution. Using ammonia pH is adjusted to 7 and temperature of the solution is increased to 200 $^{\circ}$ C. The water molecules started evaporating from the solution and the sticky mass began to bubble. The temperature of the beaker was increased to 380 $^{\circ}$ C in order to increase reaction rate. Later several minutes, gel automatically ignited and burnt with glowing flints. The auto ignition was completed within minute yielding brown colored ashes. The prepared powder was annealed at 500 $^{\circ}$ C for 10 hrs to get the final product. This method is mostly used in manufacture of Na-ion batteries. (Litao et al).

VIII. NANO-ILMENITE MATERIALS AND APPLICATIONS

A. Application of Nano Ilmenites in dye Removal

Dyes are the chemical substances which are contributing to environmental pollution. These are released into the environment by the textile industry, pharmaceutical industries, etc. Dyes are very toxic, teratogenic, and mutagenic and hence they are causing a serious threat to all the living organisms. Removal of dyes from industrial wastes is the most important environmental concern. Generally dyes are resistant to biodegradation. So to remove them effectively, environmental friendly materials are needed.

The catalytic properties of nano-ilmenites are studied in three plates under which each plate contain 10 μ L of each dye with different colors and 5ml of distilled water is added to each plate with 0.1g of nano ilmenite particles. One plate is used as blank, without addition of catalytic ilmenite. These plates have been exposed to UV light for 30 min and the color changes were recorded at 465,624,540 nm for comassie Blue, Malachite green and alkaline fusion respectively. Dyes removal is determined by changes in absorbance. (Using Milton Roy Spectrometer 21D). Nano-ilmenites show high catalytic activity and removed all dyes. Regarding Alkaline Fusion nano-ilmenites removes 50% of the color in both light and dark condition. (Samira et al).

B. Removal Of Color From Oil Using Nano-Ilmenites

In order to investigate the effect of nano-ilmenites on kerosene, it was exposed to nano-ilmenites for 21 days. Then the changes in the color were determined and absorbance of kerosene was measured at 420 wavelengths by Milton Roy Spectrometer 21D.

C. Nano-Ilmenites Role In Sodium-Ion Batteries

In order to reduce carbon dioxide emission, renewable resources came into existence. These energy resources require energy conversion and the energy is stored from off-peak electricity. The stored energy is released during on-peak period. Batteries are the most appropriate electricity supply system. It has the advantage of stability, reliability, and efficiency. Apart from lithium batteries, sodium-ion batteries (SIBs) have the same physical properties, low cost and abundant resource. Hence they are re-highlighted for next generation large scale storage systems. There are many types of materials used as SIBs anode candidates. They include Sb and Sn. Ilmenite has both Fe and Ti ions approximately of equal size, this bimetal oxide (which contains two metal elements) have great properties like ion storage, catalytic activity and gas sensors. The nano-ilmenites were embedded in carbon nano tubes which were synthesized by annealing process of TiO_2 coated metal organic frameworks. During the annealing process, the tiny ilmenite nano particles were fully embedded in the in situ formed carbon nano tubes. This obtains nano particle embedded carbon nano tubes with high surface area, stable structure and excellent electric conductivity. When they are utilized as sodium ion battery anodes they present remarkable rate capability, cycle stability and high columbic efficiency of 99% approximately.

IX. POSSIBLE APPLICATIONS OF THESE ILMENITES AS NANO MATERIALS

Nano technology can be called as a revolution in various fields like industrial sectors, information technology, home land security, energy, food safety, transportation, medicine, environmental sciences. Nano materials have high surface area to volume ratio. This property makes them move chemically reactive properties like heat resistance, electronic, magnetic and catalytic properties. Some of the material applications of nano materials are as follows:

- 1) Nano scale additives to or surface treatments of fabrics.
- 2) Nano scale films are used on camera display, computer, eye glasses.
- 3) It is used in lightening of cars, airplanes, boats, trucks, spacecrafts etc and thereby reduces fuel consumption.
- 4) Used in motorcycle helmets, tennis rackets, luggage, automobile parts, etc.
- 5) Nano Bio-engineering is a branch of science which aims to enable conversion of cellulose from wood chips, corn stalks into ethanol for fuel.
- 6) Lubricants, oils enabled by nanotechnology reduce wear and tear thereby increases the lifetime of moving parts from power tools to industrial machinery.
- 7) Nano particles are extensively used as catalyst to boost chemical reaction. This reduces the quantity of catalytic material pollutants. It is widely used in automotive catalytic converters, petroleum refining.
- 8) Nano particles are used in personal care products, superior household products, stain removers etc.
- 9) Nano technology made great contributions in computing and electronics. This leads to faster, smaller and more portable systems which can manage and store larger amounts of information.
- 10) Nano technology is being studied about the diagnosis and treatment of atherosclerosis. It is also used in diagnostic tools and better imaging. It also improves vaccines; include vaccine delivery without use of needles.

A. Applications of Ilmenites from East Coast of India:

Ilmenites from East Coast of India in the state of Tamil Nadu have various applications as nano materials. As Titanium (Ti) metal: Used in aerospace, and aviation industry, chemical industry, surgical equipments, bullet proof vests, electrical turbines tubing, different alloys in iron and steel industry, immersion heater tubes, spectacle frames, consumer goods and golf clubs. Also used for coating of welding electrodes.

X. CONCLUSION

Nano technology is the future science which has many contributions in varied fields. Industries, research, health and medicines are some fields in which the usage of beach placers is very well known. Now-a-days a new invention in the name of Nano Technology started to speedup the present technology and gives fruitful results. Geology is not an exemption to these sciences. India is gifted with many placer deposits along the East Coast of India. Among these ilmenite is one such mineral which has wide range of applications. Various types of ilmenite deposits along the East Coast of India were studied along with their characterization. Synthesizing nano ilmenites from these deposits and applied to material sciences gives tremendous results as these particles have special properties. Usage of nano ilmenites reduces the material consumption, time, pollution and increases the reaction rate, life time of the products.

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