SYNTHESIS AND CHARACTERIZATION OF CHROMIUM AND MANGANESE OXIDES

A DISSERTATION

Submitted in partial fulfillment of the
requirements for the award of the degree
of
MASTER OF TECHNOLOGY
in
ADVANCED CHEMICAL ANALYSIS

By

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CERTIFICATE

I hereby certify that the work entitled " **SYNTHESIS AND CHARACTERIZATION OF MANGANESE AND CHROMIUM OXIDES**" has been carried out by Ms. Nidhi Virmani, Department of Chemistry, IIT Roorkee, under my supervision during August-2007 to June-2008. To the best of my knowledge the same has not been submitted elsewhere for the award of degree.

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CANDIDATE'S DECLARATION

I hereby declare that the work which is being presented in the project entitled **"SYNTHESIS AND CHARACTERIZATION OF MANGANESE AND CHROMIUM OXIDES"** in partial fulfillment of the requirement for the award of the degree of **MASTER OF TECHNOLOGY** submitted in the Department of Chemistry, IIT Roorkee is an authentic record of my own work carried out during the period from August-2007 to June-2008 under the supervision and guidance of **Prof. Kamaluddin**.

The matter embodied in this project work has not been submitted for the award of any other degree.

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ABSTRACT

In the present dissertation different oxides of chromium and manganese were prepared by the hydrolysis of their respective metal nitrates with sodium hydroxide by precipitation method. The precursor and the oxides were characterized by various analytical techniques such as TG-DTA, Powder XRD, FE-SEM, EDAX. TGA studies for chromium oxide showed a phase transition at 224^0C and for manganese oxide showed the existence of different forms at different temperature. The XRD suggests that the chromium oxide formed is CrO_2 which changes to Cr_2O_3 when heated to 500^0C either in H_2 or N_2 atmosphere but with different lattice parameters. Manganese hydroxide formed changes to Mn_2O_3 when heated at 750^0C in air whereas it changes to Mn_3O_4 when heated at 500^0C in N_2 atmosphere for 8 hours. In FE-SEM images the particles look agglomerated with irregular morphology.

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1 INTRODUCTION AND LITERATURE REVIEW

1.1 Metal Oxides

Transition metals form a wide variety of oxides. Metal oxides are protected from further oxidation by forming a hard scale of oxides when it is being oxidized. Not all metal oxides form a scale. Metal oxides are very common commodities, widely applied, and have many different varieties. For example, zinc oxide sintered together with other metal oxide additives have been made into non linear resistors, which are called Varistors for surge suppressing function. The suppressing function has been applied for switching and also for protection of random voltage.

Iron oxide and other metal oxides are used in thermite reactions, and this has been applied in many ways, including welding in spaceship repairs. Iron oxides are also the raw material for all magnets and magnetic materials used for computer disks and recording tapes[1].

Metal oxides that dissolve in water react with water to form basic solutions.

e.g. $BaO (s) + H_2O(l) \dashrightarrow Ba^{2+}(aq) + 2\ OH^-(aq)$

Whereas Nonmetal oxides react with water to form acidic solutions.

e,g. $CO_2 (g) + H_2O(l) \dashrightarrow H_2CO_3 (aq)$

$P_4O_{10} (s) + 6\ H_2O(l) \dashrightarrow 4\ H_3PO_4 (aq)$

The most simple cases are the binary oxides, like TiO_2, Fe_3O_4, NiO, OsO_4, $Fe_{0.9}O$, ReO_3, etc. The number of compounds is already large and used as insulators, magnetic oxides, semiconductors, metals.

Ternary oxides, like Fe_2CoO_4, $LaNiO_3$, $PbTiO_3$, $SrTiO_3$ are generally dielectric materials

Complex oxides, like $YBa_2Cu_3O_7$, $Tl_2Ba_2Ca_2Cu_3O_{10}$. These examples are high-temperature superconductors.

1.1.1 Structural Families

Table 1: The structural details of different types of metal oxides with examples [2] :

Formula	**Coordination**	**Name**	**Symmetry**	**Examples**
M_2O	2 : linear 4 : tetrahedral	Cuprite Antifluorite	cubic cubic	Cu_2O Na_2O
MO	6 : octahedral 4 : tetrahedral 4 : planar 4 : pyramidal	Rocksalt wurtzite PdO PbO	cubic hexagonal tetragonal tetragonal	MgO, NiO ZnO PdO SnO, PbO
M_3O_4	Two M6(oct); one M4(tet)	Spinel	cubic	Fe_3O_4
M_2O_3	6 : octahedral	Corundum	hexagonal	α- Al_2O_3, Ti_2O_3
MO_2	8 : cubic 6: octahedral	Fluorite Rutile	cubic tetragonal	ZrO_2, UO_2 TiO_2, SnO_2
M_2O_5	5+1;distorted	V_2O_5	orthorhombic	V_2O_5
MO_3	6 : octahedral 6 : distorted	ReO_3 MoO_3	Cubic monoclinic	ReO_3, WO_3 MoO_3
AMO_3	M6, A12 M and A6 (oct)	Perovskite Ilmenite	Cubic trigonal	$SrTiO_3$, $BaTiO_3$ $LiNbO_3$
A_2MO_4	M6, A12	Layer perovskite	Tetragonal or distorted	La_2CuO_4

1.2 Synthesis of Metal Oxides

Most elements will react with oxygen at appropriate temperature and oxygen pressure conditions, and many oxides may thus be directly prepared. Most metals in massive form react with oxygen only slowly at room temperatures because the first thin oxide coat formed protects the metal. The oxides of the alkali and alkaline-earth metals, except for beryllium and magnesium, are porous when formed on the metal surface, and they provide only limited protection to the continuation of oxidation, even at room temperatures. Gold is exceptional in its resistance to oxygen, and its oxide (Au_2O_3) must be prepared by indirect means. The other noble metals, although ordinarily resistant to oxygen, react at high temperatures to form gaseous oxide.

Some of the important chemical method of synthesis of oxides are co precipitation and precursor method, ion exchange and alkali flux method, sol-gel method, topochemical method, electrochemical method, high pressure method (including hydrothermal synthesis) and combustion method.

Some of the typical reactions that occur in oxide synthesis:

$YBa_2Cu_3O_6(s) + O_2(g) \rightarrow YBa_2Cu_3O_7(s)$

$ZnO(s) + Fe_2O_3(s) \rightarrow ZnFe_2O_4(s)$

$BaO(s) + TiO_2(s) \rightarrow BaTiO_3(s)$

$ZnS(s) + CdO(s) \rightarrow CdS(s) + ZnO(s)$

$LiFeO_2(s) + CuCl(l) \rightarrow CuFeO_2(s) + LiCl(s)$

Another route is to obtain a solid product from a gas phase reaction. MgO and Cr_2O_3 do not react to form $MgCr_2O_4$, but Cr_2O_3 reacts with O_2, giving $CrO_3(g)$, which can react with MgO

$MgO(s) + Cr_2O_3(s) \rightarrow O_2 \rightarrow MgCr_2O_4(s)$

Obtaining the correct phase often requires adjustment of the oxygen content. This can be done by annealing in a H_2/N_2 mixture or a CO/CO_2 mixture. In simple cases annealing in argon or nitrogen may be sufficient. Hydrogen anneal would have the following effect:

$M_2O_3(s)+H_2(g) \rightarrow 2MO(s) + H_2O(g)$

Cation substitutions are also common. Typically this can be done if ionic radii match and charge neutrality is maintained. For example, partial substitutions can be made in $YBa_2Cu_3O_7$, replacing Y with Ca and Ba with La.

1.2.1 Ceramic Method

The ceramic method is most commonly employed to prepare solid materials. The procedure involves powders of oxide, carbonates, oxalates, etc. are mixed, possibly pelletized, and annealed. Annealing conditions are selected based on *phase diagrams*. Reaction usually occurs in an alumina, silica or platinum crucibles. If volatile components are present, reaction has to be performed in sealed capsules. Reaction temperatures are relatively high. Resistive furnaces go about 1500^0C, ark and skull heating up to about 3000^0C and laser heating to 4000^0C or more.

Problems with the ceramic synthesis technique:

- If no melt forms during reaction, the whole process must happen in solid state and depends on very slow diffusion. Reaction starts at points of contact between constituents. Particles have finite size, reaction becomes slower as the reaction front moves deeper into particles.

- Only way to verify that the reaction has finished is to take periodic x-ray diffraction measurements or analyze the product in someother way.

- Difficult to guarantee a single-phase product.

- Different phases in the product are hard or impossible to separate.

Despite of these shortcomings the technique is widely used and quite successful for cation substitution reactions.

Improvements can be obtained by smaller particle size (< 1 μm instead of 10 μm), e.g. by

Spray-drying, freeze-drying, co-precipitation.

1.2.2 Precursor Method

The diffusion length problem of solid-state reactions can be avoided if the necessary cations can be included in a suitable precursor. Oxide is formed by the decomposition of the precursor:

Precursor	Product
$LaCo(CN)_6 \cdot 5H_2O$	$LaCoO_3$
$LaFe(CN)_6 \cdot 6H_2O$	$LaFeO_3$
$Ba[TiO(C_2O_4)_2]$	$BaTiO_3$
$Li[Cr(C_2O_4)_2(H_2O)_2]$	$LiCrO_2$
$M_3Fe_6(CH_3\text{-}COO)_{17}O_3OH \cdot 12C_5H_5N$	MFe_2O_4 spinels

Organometallic precursors, especially carboxylates and alkoxides, used for synthesis of some of the perovskite oxides have been reviewed by Chandler et al. [3]. Many metals can be combined in a precursor by using carbonates. Various carbonates have a similar calcite structure and can be readily prepared as solid solutions. During heating in nitrogen or vacuum, an oxide $Mn_{1-x}M_xO$ is formed. The oxide has a rock salt structure. Metals that have been used include Mg, Mn, Fe, Zn, Ca, Co, Cd. The simple oxides can be used as precursors for further synthesis.

1.2.3 Topochemical reactions

Solid state reactions in oxides are often *topochemical*, i.e. the reactivity is controlled by the crystal structure, not the chemical nature of the constituents and involves the introduction of a guest (or removal) species into the lattice, resulting in significant structural modification.

For eaxmple the dehydration reaction of $WO_3 \cdot 1/2H_2O$

Oxide reduction reaction ABO_3 to $A_2B_2O_5$ are also topochemical. For example, reduction of $LaNiO_3$ can results in members of a homologous series of compounds $La_nNi_nO_{3n-1}$. The most stable member of this series is obtained by controlled reduction in hydrogen at 600 K, yielding n = 2, $La_2Ni_2O_5$. This oxide can be reoxidized at a lower temperature. Note that $La_2Ni_2O_5$ can not be formed by a solid state reaction of La_2O_3 and a metal oxide.

1.2.4 Intercalation Method

Insertion of a guest ion or molecule into a solid host lattice without major rearrangement of the solid structure. Typically happens in layered oxides where bonding within a layer is strong but weak between layers. An example is Li intercalation in TiO_2, ReO_3, Fe_2O_3, Fe_3O_4 or Mn_3O_4. Easy deintercalation of Li from LiMO2 is why these oxides are used in lithium cells. Intercalation reactions can be used as a synthesis tools, e.g. lithium-intercalated anatase $Li_{0.5}TiO_2$ transforms at 770 K into superconducting $LiTi_2O_4$.

We have already looked at alkali earth-intercalated WO_3 and MoO_3 phases.

Examples of Li intercalation in oxide hosts

Host	Description
MO_2	Li_xMO_2 ($x = 1$) M=Mo, Ru, Os, Ir. MO_2 has the rutile structure
TiO_2	Li_xTiO_2($0 < x < 0.7$) converts irreversibly into a spinel $LiTi_2O_4$ at 770 K
CoO_2	Li_xCoO_2 ($0 < x < 1$) various phases obtained by delithiating $LiCoO_2$
VO_2	Li_xVO_2 ($0 < x < 1$)

Fe_2O_3	$Li_xFe_2O_3$ ($0 < x < 2$) anion array changes from hcp to ccp
Fe_3O_4	$Li_xFe_3O_4$ ($0 < 2$)
Mn_3O_4	$Li_xMn_3O_4$ ($0 < x < 1.2$) intercalation suppresses the tetragonal distortion
MoO_3	Li_xMoO_3 ($0 < x < 1.55$)
V_2O_5	$Li_xV_2O_5$ ($0 < x < 1.1$)
ReO_3	Li_xReO_3 several phases depending on x

Hydrogen can be intercalated into various oxides.

Iodine has been intercalated into high-Tc oxides like $Bi_2CaSr_2Cu_2O_8$ without destroying superconductivity.

1.2.5 Sol-gel synthesis

Sol-gel synthesis avoids the problems of powder ceramic synthesis. The process involves these (approximate) steps:

1. Prepare a *sol*: a colloidal suspension of inorganic precursor in a liquid, such as alkoxysilanes.
2. Adjust the pH of the solution to promote the formation of a *gel*
3. Dry the gel, forming a xerogel (or an aerogel or cryogel)
4. Sinter

Advanatages of the sol-gel technique:

- Precursors are very finely mixed
- Relatively easy to adjust the stoichiometry
- Can be used for coatings, thin films
- Due to the small particle sizes, processing temperatures can be relatively low.

1.2.6 High-pressure synthesis

Up to 10 kbar

Moderately high pressures can be used in an open hydrothermal system, where reaction gas is under pressure (O_2, N_2, etc.) Can be used for synthesis of RhO_2, PtO_2 (high oxidation state oxides).

Closed systems use an internal oxidant, like $KClO_3$ which decomposes under reaction conditions providing the oxygen. $Re_2M_2O_7$ compounds and zero thermal expansion ceramic $Ca_{0.5}Ti_2P_3O_{12}$ can be synthesized this way (_1000 K, 3..5 kbar).

10 to 50 kbar

Piston-cylinder type presses are used with integrated heaters. Temperatures of around 1800 K can be used. The pressure chamber may be made of tungsten carbide. Sample is in a metal capsule, sample size can be around 0.1 cm^3.

over 50 kbar

Multianvil or belt pistion presses can reach 150 kbar or more and very high temperatures of over 2000 K. Sample sizes are a few mm3.

High pressures are used for the synthesis of phases that would not otherwise form. The free energy is affected by the following processes

1. Pressure delocalizes outer d electrons by increasing orbital overlap
2. Pressure stabilizes higher valence states. For example, iron oxidizes to Fe^{4+} and it is possible to prepare $CaFeO_3$.
3. Pressure affects magnetic ordering and thus the electronic structure
4. Cations can enter different lattice sites under pressure. At ambient pressure we get a spinel $A[AMn]O_4$ (A=Mg, Co, Zn) because the 2+ ions prefer tetrahedral

coordination. At high pressure the $A^{2+}Mn^{4+}O_3$ phase forms where all ions are in octahedral sites.

5. High pressure stabilizes more close packed phases (higher coordination). These can occasionally be quenched to ambient pressure.
6. Solid state reactions are much faster under pressure (hours instead of days for $LnFeO_3$, $LnRhO_3$, $LnNiO_3$) [4].

1.2.7 Ion exchange Method

Ion exchange in fast ion conductors such as β-alumina is well known. The exchange can be carried out in aqueous or in molten salt conditions. Thus sodium β-alumina has been exchanged with H_3O^+, NH_4^+ and other monovalent and divalent cations giving rise to different β-aluminas.

Typical examples are:

α-$NaCrO_2$ → α-$LiCrO_2$ (in presence of $LiNO_3$, 570K;24h)

$KAlO_2$ → β-$AgAlO_2$ (in presence of $AgNO_3$(l))

α-$LiFeO_2$ → $CuFeO_2$ (in presence of CuCl(l))

The structure of the frame is largely retained during ion exchange except for minor changes to accommodate the structural preferences in the incoming ion.

Recently $LiMnO_2$ has been prepared by the ion exchange reaction of $NaMnO_2$ and LiCl or LiBr in hexagon [5].

1.2.8 Alkali Flux and Electrochemical Method

Use of strong alkaline media in the form of either solid fluxes or molten solutions has enabled the synthesis of novel oxides. The alkali flux stabilizes higher oxidation states of the metal by providing an oxidizing atmosphere. Alkali carbonate fluxes have been used to prepare transition metal oxides such as $LaNiO_3$. For example $La_4Ni_3O_{10}$ was prepared by bubbling Cl_2 gas through an NaOH solution of lanthanum and nickel nitrates.

Electrochemical methods have been employed to advantage for the synthesis of many solid materials, including oxides. Vanadate spinels of the formula MV_2O_4 as well as tungsten bronzes (A_xWO_3), have been prepared by the electrochemical route.[6] Tungsten bronzes are obtained at the cathode when current is passed through two inert electrodes immersed in a molten solution of the alkali metal tungstate A_2WO_4 and WO_3; oxygen is liberated at the anode. Oxides containing metals in high oxidation states are prepared by electrochemical methods(e.g. $La_{1-x}Sr_xFeCO_3$)

1.2.9 Crystal Growth Method

Most of the techniques discussed above result in powder samples. It is often necessary to obtain single crystals. The basic methods for that are Single component

1. Solid-solid
2. Liquid-solid
   - Directional solidification (Bridgman-Stockbarger)
   - Cooled seed (Kyropoulos)
   - Pulling (Czochralski and tri-arc)
   - Horizontal or vertical zoning
   - Flame fusion (Verneuil)
   - Slow cooling in a skull
3. Gas-solid (sublimation and sputtering)

1.3 Magnetic Properties of Metal Oxides

Table 2: The more important properties of oxides including magnetic, electrical, dielectrical and optical properties are discussed briefly.

Metal Oxides	Properties
TiO, V_2O_5, Nb_2O_5, HfO_2, Ta_2O_5, WO_3, MoO_3	Diamagnetic semiconductors or insulators when pure, but exhibit n-type extrinsic conduction when doped or slightly reduced
TiO, NbO, CrO_2, RuO_2, OsO_2, MoO_2, RhO_2, WO_2, IrO_2, ReO_3	Metallic and pauli paramagnetic (CrO_2 is paramagnetic)
Ti_2O_3, Ti_3O_5, Ti_4O_7, V_2O_3, V_3O_5, VO_2, NbO_2	Exhibit temperature-induced metal to non metal transition
MnO, FeO, CoO, NiO, Cr_2O_3, Fe_2O_3, Mn_3O_4	Insulators

1.4 Applications of Metal Oxides

Metal-oxides are emerging as technically important materials because of the wide variety of physical properties they possess, which make them attractive for applications such as photovoltaic devices, gas sensors, microelectronics and corrosion protection devices. Some of them are described below:

1.4.1 Catalyst

The transition-metal oxides act as catalysts for the magnesium-hydrogen reaction. Cr_2O_3 yields the fastest hydrogen absorption, whereas V_2O_5 and Fe_3O_4 cause the most rapid desorption of hydrogen. The primary focus of catalytic reactions with manganese oxides has been in the area of oxidations. When sonochemically prepared iron oxide was used as a catalyst for oxidation of cyclohexane with oxygen (1 atm) and at 70°C, cyclohexanol and cyclohexanone were obtained (16.5% conversion, 90% selectivity). With amorphous cobalt oxide (Co_3O_4) as a catalyst a conversion of 4–5% of cyclohexane was achieved. It is well known that titanium oxide is an efficient oxygen activator and at the same time it can be used as a carrier for transition metal catalysts by promoting their stability and reactivity due to metal-support interaction [7]

The other reactions catalysed by manganese oxides include decomposition of several reactants. Amorphous manganese oxide materials have been found to photochemically and thermally decompose phosphine oxide materials that are model complexes for chemical warfare agents.Also they have been used as catalyst for decomposition of H_2O_2 [8], for selective oxidation of cyclohexane to cyclohexanol and cyclohexanone [9], and also for the oxidative dehydrogenation of ethanol.[10] Also iron oxide has been studied as a selective catalyst for the production of butadiene in the partial oxidation of butane. The catalytic properties of iron and zinc cations for the water gas shift reaction : ($CO + H_2O \rightarrow CO_2 + H_2$) are also observed [11]. The catalytic dehydration of ethanol to ethylene was investigated using different transition metal oxides such as titanium oxide, magnesium oxide, cobalt oxide, chromium oxide [12] etc. TiO_2 is used as a photocatalyst because of its high catalytic activity.

1.4.2 Adsorbent

Several metal oxides such as SiO_2, Al_2O_3, TiO_2 and ZnO_2 adsorb H_2S and CH_3SH and resulting changes in surface acidity were studied by Travert *et al.* [13] through IR spectroscopy using Co (at 77 K) and 2,6-dimethylpyridine (dmp) at 300K as probe molecule. In a process for removing oxygen from an inert gas comprising oxygen containing inert gas stream through an adsorbent bed under conditions for removing oxygen, the improvement which comprises removing trace oxygen from the inert gas stream utilizing an adsorbent comprising a porous reducing support impregnated with an alkali metal oxide or an alkaline earth metal oxide of about 10% to about 90% by weight

1.4.3 Sensor

Metal oxides based chemical sensors are devices that translate the changes in the concentration of gaseous chemical species into electrical signals, generally changes of resistance/conductance. A sensor element normally comprises the following parts: a) Sensitive layer deposited over a b) Substrate provided with c) Electrodes for the measurement of the electrical characteristics. The device is generally heated by its own d) Heater; this one is separated from the sensing layer and the electrodes by an electrical insulating layer. The base of the gas detection is the interaction of the gaseous species at the surface of the semiconducting sensitive metal oxide layer.[14] Metal–metal oxide electrodes provide robust and miniaturised pH sensors. Iridium oxide electrodes are best used. The metal oxide semiconductor (MOS) sensors developed by Applied Sensor use tin oxide based sensing thick films. The MOS sensors show high sensitivity, good stability, long lifetime, and short response/recovery times. The sensors can be operated in a wide ambient temperature range (-40°C to +70°C) and humidity range (0 to 100% RH without condensation), and do not require maintenance. The micro sensors have small size and low power consumption, making them suitable for applications in handheld devices. The application range for MOS sensors covers various fields such as: automotive, packaging and food control, medical, security, process control.

Metal oxide sensors are commonly used to monitor a variety of toxic and inflammable gases in air pollution monitoring system, food industry, medical diagnostic equipment and gas leak alarms. Electrochemical sensors using stabilized zirconia and oxide electrodes were tested by Miura *et al.* [15] for detecting NO and NO_2 potentiometrically and amperometrically at high temperature.

1.4.4 Electrode

Several transition metal oxides are used as electrode materials. Among several transition metal oxide electrode materials for supercapacitors, hydrous ruthenium oxide shows a high capacity of over 700 F/g [16] and excellent cyclability in aqueous sulphuric acid. Because of its high cost, alternative metal oxide electrode materials are being developed to replace ruthenium oxide e.g., NiO_x, CoO_x, MnO_2 etc. Lithium intercalation and deintercalation in amorphous MoO_3 electrodes was investigated in situ using grazing incidence reflection mode X-ray absorption spectroscopy. Iron based oxide such as $LiFeO_2$ is regarded as a positive electrode material for lithium ion battery [17]. Metal electrode coated by thin oxide film (e.g. PtO_x on Pt, TiO_2 on Ti) is frequently encountered in electrochemical measurement. Li-Fe-Mn positive electrode is used in automobiles. Solid oxide fuel cell which is a ceramic device that operates at temperature range 800-1000 C. The design based on zirconia electrolyte with (La, Sr) MnO_3 is preferred as cathode and Ni/ ZrO_2 as anode [18].

1.5 Chromium

Chromium is a chemical element which has the symbol **Cr** and atomic number 24. It is a steel-gray, lustrous, hard metal that takes a high polish and has a high melting point. It is also odourless, tasteless, and malleable. Chromium was named after the Greek word "Chrôma" meaning color, because of the many colorful compounds made from it.

1.5.1 Occurrence of elemental Chromium

Chromium is mined as chromite ($FeCr_2O_4$) ore. About two-fifths of the chromite ores and concentrates in the world are produced in South Africa

Though native chromium deposits are rare, some native chromium metal has been discovered. The Udachnaya Mine in Russia produces samples of the native metal. This mine is a kimberlite pipe rich in diamonds, and the reducing environment so provided helped produce both elemental chromium and diamond.

Chromium is obtained commercially by heating the ore in the presence of aluminium or silicon.

1.5.2 Isotopes

Naturally occurring chromium is composed of three stable isotopes; ^{52}Cr, ^{53}Cr, and ^{54}Cr with ^{52}Cr being the most abundant (83.789% natural abundance). Nineteen radioisotopes have been characterized with the most stable being ^{50}Cr with a half-life of (more than) $1.8\text{x}10^{17}$ years, and ^{51}Cr with a half-life of 27.7 days. All of the remaining radioactive isotopes have half-lives that are less than 24 hours and the majority of these have half-lives that are less than 1 minute. This element also has 2 meta states.

^{53}Cr is the radiogenic decay product of ^{53}Mn. Chromium isotopic contents are typically combined with manganese isotopic contents and have found application in isotope geology. Mn-Cr isotope ratios reinforce the evidence from ^{26}Al and ^{107}Pd for the early history of the solar system. Variations in ^{53}Cr/^{52}Cr and Mn/Cr ratios from several meteorites indicate an initial ^{53}Mn/^{55}Mn ratio that suggests Mn-Cr isotope systematics must result from in-situ decay of ^{53}Mn in differentiated planetary bodies. Hence ^{53}Cr provides additional evidence for nucleosynthetic processes immediately before coalescence of the solar system.

The isotopes of chromium range in atomic weight from 43 u (^{43}Cr) to 67 u (^{67}Cr). The primary decay mode before the most abundant stable isotope, ^{52}Cr, is electron capture and the primary mode after is beta decay.

1.5.3 Physical Properties

Chromium with atomic mass 51.99611 have boiling point 2945K and melting point 2180K. Its density is 7.19 gcm^{-3}

1.5.4 Chemical Properties

Chromium is a member of the transition metals, in group 6. Chromium(0) has an electronic configuration of $4s^13d^5$, due to the lower energy of the high spin configuration. Chromium exhibits a wide range of possible oxidation states. The most common oxidation states of chromium are +2, +3, and +6, with +3 being the most stable. +1, +4 and +5 are rare. Chromium compounds of oxidation state +6 are powerful oxidants.

Chromium is passivated by oxygen, forming a thin (usually a few atoms thick being transparent because of thickness) protective oxide surface layer with another element such as nickel, and/or iron. It forms a compound called a spinel structure which, being very dense, prevents diffusion of oxygen into the underlying layer. (In iron or plain carbon steels the oxygen actually migrates into the underlying material.) Chromium is usually plated on top of a nickel layer which may or may not have been copper plated first. Chromium as opposite to most other metals such as iron and nickel does not suffer from hydrogen embrittlement. It does though suffer from nitrogen embrittlement and hence no straight chromium alloy has ever been developed. Below the pourbaix diagram can be seen, it is important to understand that the diagram only displays the thermodynamic data and it does not display any details of the rates of reaction.

1.5.5 Chromium Compounds

Potassium dichromate is a powerful oxidizing agent and is the preferred compound for cleaning laboratory glassware of any trace organics. It is used as a saturated solution in concentrated sulfuric acid for washing the apparatus. For this purpose, however, sodium dichromate is sometimes used because of its higher solubility (5 g/100 ml vs. 20 g/100 ml respectively). Chrome green is the green oxide of chromium, Cr_2O_3, used in enamel painting, and glass staining. Chrome yellow is a brilliant yellow pigment, $PbCrO_4$, used by painters.

Chromic acid has the hypothetical structure H_2CrO_4. Neither chromic nor dichromic acid is found in nature, but their anions are found in a variety of compounds. Chromium trioxide, CrO_3, the acid anhydride of chromic acid, is sold industrially as "chromic acid".

1.5.6 Uses of Chromium

In metallurgy, to impart corrosion resistance and a shiny finish. Chromium(III) oxide is a metal polish known as green rouge. Chromium salts color glass an emerald green. Chromium is what makes a ruby red, and therefore is used in producing synthetic rubies, also makes a brilliant yellow for painting. Chromite is used to make molds for the firing of bricks. Chromium salts are used in the tanning of leather. Potassium dichromate is a chemical reagent, used in cleaning laboratory glassware and as a titrating agent. It is also used as a mordant (i.e., a fixing agent) for dyes in fabric. Chromium(IV) oxide (CrO_2) is used to manufacture magnetic tape, where its higher coercivity than iron oxide tapes gives better performance.

1.6 Oxides of Chromium

There are four oxides of Chromium:

Chromium(II) oxide, CrO

Chromium(III) oxide, Cr_2O_3

Chromium dioxide (chromium(IV) oxide), CrO_2

Chromium trioxide (chromium(VI) oxide), CrO_3

1.6.1 Chromium(II) oxide, CrO

It's a black insoluble powder which is prepared by oxidizing chromium amalgam with air. At high temperature hydrogen reduces it to the metal.

1.6.2 Chromium(III) oxide, Cr_2O_3 (chromic oxide, chromium sesquioxide)

It's a green powder that is isomorphous with iron(III) oxide and aluminium(III) oxide. It is prepared by gently heating chromium(III) hydroxide or by heating ammonium dichromate. It is used as a pigment in the paint and glass industries. Chromic oxide (Cr_2O_3) is a wide-band-gap ($Eg = 3$ eV) [19] *p*-type semiconductor [19-22]. There is a great interest in the synthesis of wide-band-gap semiconductors, since they have many possible applications in optical and electronic devices. Although Cr_2O_3 is a *p*-type semiconductor, it shows high electrical conductivity with partial or complete electron transfer [21]. Cr_2O_3 is also an important refractory material because of its high melting temperature (2300°C) and high-temperature oxidation resistance [23]. It is essential for preparing nanocrystalline ceramics for providing high-temperature corrosion resistance, which can be used in high-temperature devices. Supported Cr_2O_3 is a promising catalyst in oxidative dehydrogenaties [24]. Cr_2O_3 nanowires can be synthesized by sol-gel template method. The room temperature photoluminescence spectrum of the Cr_2O_3 nanowires shows light emission in the UV region. The as-synthesized Cr_2O_3 semiconductor nanowires with high-temperature oxidation resistance and UV-emitting properties make it a good candidate material in optical memory system used as CD read head, which can be operated in high-temperature condition [25].

1.6.3 Chromium dioxide, CrO_2

It's a black solid which is prepared by heating chromium(III) hydroxide in oxygen at a temperature of 300^0-350^0C. This oxide has been very unstable. The reaction $CrO_3 + 2NH_4X \rightarrow CrO_2 + 2\ NH_3 + H_2O + X_2$ (X = Br, I), which occurs quantitatively at 120–150°C, provides a convenient method for the synthesis of CrO_2

Chromium (iv) oxide, CrO_2, is unique among the rutile-type transition metal dioxides [26], exhibiting ferromagnetic (Tc = 395 K) and metallic properties [27]. Because of these properties, the material finds application as a magnetic recording medium in the form of tapes. In recent years, there has been a renewed interest in this material in view of the realization [28] that it is a 'half-metallic' ferromagnet. Since CrO_2 is a metastable phase [27] (decomposing at > 288°C at 1 atm pressure of O_2), all the methods reported for its synthesis require high pressures [27]. Hydrothermal decomposition of aqueous solutions of CrO_3 at elevated temperatures and pressures (typically 480°C and 2 kbar) is a common method for the synthesis of polycrystalline CrO_2 powders [27]. Growth of single crystals [29] however require much higher temperatures (900–1300°C) and pressures (60–65 kbar).

1.6.4 Chromium trioxide, CrO_3 (chromic anhydride)

A red crystalline solid formed when concentrated sulphuric acid is added to a cold saturated solution of potassium dichromate. Chromium(IV) oxide is readily soluble in water forming a solution that contains several of the polychromic acids. On heating it decomposes to yield chromium (III) oxide. It is used as an oxidizing reagent.

1.7 Manganese

1.7.1 Occurrence of Elemental Manganese

Manganese is widespread in nature . It is found as the free element in nature (often in combination with iron), and in many minerals. The free element is a metal with important industrial metal alloy uses. Manganese ions are variously colored, and are used industrially as pigments and as oxidation chemicals. Manganese (II) ions function as cofactors for a number of enzymes; the element is thus a required trace mineral for all known living organisms. It is the 13th most abundant element, and the third most abundant transition element, after iron and titanium. The most important manganese ores are *brownstone* (e.g., pyrolusite) i.e., $MnO_{1.7\text{-}2.0}$; *braunite* Mn_2O_3. Others are *manganite* , MnO(OH) ; *hausmannite*, Mn_3O_4 ; *rhodochrosite* $MnSiO_3$. Large quantities of manganese are also found in manganese nodules on the ocean floor , which are formed by agglomeration of metal oxide colloids. They contain 15-20% Mn. The colloids in turn are formed by weathering of primary silicate sediments which are then washed into the ocean.

1.7.2 Isotopes of Manganese

Naturally occurring manganese (Z=25) consists solely of the isotope $^{55}Mn_{25}$ which is used for NMR studies. The synthetic nuclides $^{54}Mn_{25}$(electron capture, $t_{1/2}$ =303 days) and $^{56}Mn_{25}$ (beta emitter , $t_{1/2}$ = 2.567 h) are used as tracers.

1.7.3 Physical Properties

Manganese is found in four different modifications (α , β , γ and δ manganese) , of which α-manganese, with a *distorted cubic closed pack* array of metal atoms , is the stable form at room temperature. Metallic manganese is silver-grey , hard , and very brittle . It melts at 1244°C, boils at 2030° C and its density is 7.44 g/cm^3.

1.7.4 Physiological Properties

Manganese is an essential trace element which in compound form is found in all living cells. The human body contains about 0.3 mg/kg , mainly in the mitochondria, cell nuclei and bones. It is needed in the synthesis of cholesterol , mucopolysaccharides , blood clotting factors and respiratory chain phosphorylation . Manganese deficiency can lead to sterility ,among other symptoms. Excess manganese causes irritation of the respiratory passages and impairment of movement .

1.7.5 Chemical properties

Manganese is somewhat more reactive than its neighbours in the periodic system , Cr , Tc and Fe. In compact form, it is only superficially oxidised by oxygen , but in finely divided form , it burns in air to form Mn_3O_4. It does not form a passivating oxide layer.

1.7.6 Uses

The most important compounds of manganese are the oxides, MnO , Mn_2O_3 , MnO_4 , MnO_2 , potassium permanganate($KMnO_4$) . They are used in the production of pigments , metal soaps, magnets , dry cells , corrosion protection (manganophosphates) , as additives to feed and fertilizers, and as oxidising agents in organic synthesis , water treatment , exhaust gas purification , oxidimetry and medicine .

1.7.7 Manganese in compounds

In its compounds , manganese is usually in oxidation state +2 , +3 , +4 , +7 (e.g., $MnCl_2$, MnF_3, MnO_2, Mn_2O_7). However there are also compounds in which it occurs in +5 and +6 states (e.g., MnO_4^{3-}, MnO_4^{2-}) , as well as the states +1,0, -1, -2 and -3 (e.g., $Mn^{I}(CN)_6^{5}$, $Mn^{0}_2(CO)_{10}$, $Mn^{-I}(CO)_5^{-}$, $Mn^{-II}(phthalocyanin)^{2-}$ and $Mn^{-III}(NO_3)(CO)$) . The +2 and +7 oxidation states are very important. The basicity of the oxides in water decreases with increasing Mn valence , while their acidity increases . Thus Mn(II)oxide is a base anhydride while Mn(VII) oxide is an acid anhydride and Mn(IV) oxide is amphoteric . The manganese (II) ion, Mn^{2+}, is the most important oxidation state of manganese , it has half filled 3d shell and is thus isoelectronic with Fe $^{3+}$. In acid solution it is particularly stable with respect to both oxidation and reduction.

1.8 Oxides of Manganese

Table 3: Manganese combines with oxygen in molecular ratio to form various oxides, hydroxides and oxide hydroxides of Manganese[30]

Compound	Form	Remarks	Structure
MnO		$MnO_{1.0-1.12}$	NaCl
Mn_3O_4	α	$MnO_{1.33-1.41}$	*Spinel, tertragonal*
	β		*cubic*
Mn_2O_3	α	$MnO_{1.5-1.6}$	Sc_2O_3
	γ		γ- Fe_2O_3
MnO_2	α	$MnO_{1.96-2.0}$	*Orthorhombic*
	β	*Unst.*	
	γ		*rutile*
Mn_2O_7		*Unst.*	
MnOOH	α		(FeS_2)
	γ	*manganite*	*monoclinic*
$Mn(OH)_2$		*pyrochroite*	$Cd(OH)_2$

1.8.1 Manganese monoxide , MnO

It is found in nature as manganosite (NaCl structure) . It is grass green to grey powder and shows antiferromagnetism with Neel's temperature -155 °C that is type of magnetism in solids such as manganese oxide (MnO) in which adjacent ions that behave as tiny magnets (in this case manganese ions, Mn^{2+}) spontaneously align themselves at relatively low temperatures into opposite, or antiparallel, arrangements throughout the material so that it exhibits almost no gross external magnetism. It is insoluble in water but readily dissolves in acids , giving pale pink solutions of Manganese(II) salts. Manganese monoxide, MnO, is used as a starting material for the production of manganous salts, as an additive in fertilizers, and as a reagent in textile printing.

MnO is produced on heating the higher oxides in flowing oxygen or upon thermal decomposition of Mn(II) carbonate or oxalate in H_2 or N_2 atmosphere [31]. Also it is produced from manganese dioxide and coke at 400-1000°C. Decomposition of $Mn_2(CO)_8$ also gives MnO with Mn_2O_3 as impurity [32]. MnO nanocrystals capped with organic ligands is prepared by decomposition of manganese acetate in a mixture of trioctylamine and oleic acid [33]. MnO is also prepared by decomposition of Manganese acetylacetonate in oleylamine [34]. MnO with average diameter 6-14 nm has been prepared by decomposition of manganese cupferronate $\{Mn(C_6H_5N_2O_2)_2\}$ in presence of trioctylphosphineoxide (TOPO) under solvothermal conditions [35]. Decomposition of $Mn(cup)_2$ at 325°C in toluene in presence of TOPO as capping agent gives MnO.

1.8.2 Dimanganese Trioxide

Mn_2O_3(manganese sesquioxide) is obtained in its α – form , on heating Mn(IV) oxide in air to above 550°C,as brown powder. On further heating to over 900°C, it is converted into reddish brown **trimanganese tetraoxide, Mn_3O_4** (manganese (II,III) oxide , $Mn^{II}Mn_2^{III}O_4$) , which is found in nature as hausmannite.The black γ-form of Mn(III) oxide is obtained by oxidation of freshly precipitated $Mn(OH)_2$ in air followed by drying the resulting hydrate $Mn_2O_3.xH_2O$, above 500°C . An intermediate hydrate is **manganese oxide hydroxide MnO(OH)** ($=Mn_2O_3.H_2O$) . The latter occurs in nature as manganite. At 300 – 500 °C ,MnO(OH) is converted to Mn_5O_8 which can also be obtained by heating Mn_3O_4 in air at 250-550 °C [31].

Manganese (II) acetylacetonate $[CH_3COCH=C(O)CH_3]_2Mn$ and manganese (III) acetylacetonate $[CH_3COCH=C(O)CH_3]_3Mn$ are dissolved in acetone at room temperature. The SBA-15 powder is then added into solution after Mn compounds have dissolved completely. The precursors are obtained by stirring until solvent evaporates. The obtained precursor is then washed with acetone. This is followed by calcination in air at 773K for 5 hours with 1K/minute as the ramping rate. This way Mn_2O_3 and Mn_3O_4 are formed.[36]

Dissolution of Mn(II) acetate in N,N'-dimethylformamide(DMF) and water gives rise to homogeneous nanocrystals like rods. Reduction of higher manganese oxides using methane as a reducing gas under controlled temperature.

1.8.3 Manganese Dioxide

The most stable and the most important Mn(IV) compound is manganese dioxide $\mathbf{MnO_2}$. It is found in nature in pure form (β-MnO_2) as grey black pyrolusite. It is an important component of brownstones, which also contain manganomelanins(α-MnO_2 with admixtures of water and cations) and ramsdellite (γ-MnO_2) [31].

MnO_2 can be prepared by treating natural brownstone with sulphuric acid ; this oxidizes the Mn^{3+} [31] :

$$Mn_2O_3 + H_2SO_4 \rightarrow MnO_2 + MnSO_4$$

Reduction of Mn(VII) salts with appropriate reducing agents like H_2O_2, sodiumthiosulphate, NH_4OH etc.

e.g. $NaMnO_2$ reduced by fumaric acid [39].

Directly mixing potassium permanganate polyelectrolyte aqueous solutions: Polyelectrolyte is used both as a reducing agent as well as protective agent. Poly(allylaminehydrochloride) i.e. PAH and Mn are mixed in a ratio 4:1 at room temperature to form MnO_2 [40].

Hydrothermal process [41] of preparing MnO_2: $MnSO_4$ is dissolved in water and sodium dodecyl sulphate (SDS) is slowly added with vigorous stirring. The resulting transparent solution is then transferred to a Teflon-lined stainless steel autoclave(50 mL) . The autoclave is sealed and maintained at 150°C for 12 hours. The product is then cooled to room temperature. The black precipitate of MnO_2 is filtered, washed with water and ethanol and finally dried at 60°C in air. Hydrothermal reaction between Mn_2O_3 and NaOH for a long duration also gives MnO_2 [42].

1.8.4 Applications of Manganese Oxide

MnO_2 is used as depolarizer in dry cells(especially zinc-carbon and Leclanche' cells) , as a pigment for bricks(red to brown to grey) , as an oxidizing agent (e.g. for producing hydroquinone from aniline , or in the production of polysulphide rubbers) , as a catalyst for oxygen transfer , in the production of manganese (II) salts such as $MnSO_4$ and as glassmaker's soap. These oxides are used as electrochromic materials. They have a wide range of applications in catalysis and battery technologies [43]. Among the series of manganese oxides Mn_3O_4 is known to be an active catalyst in various oxidation and reduction reactions e.g., it can be used as a catalyst for the oxidation of methane and carbon monoxide or the selective reduction of nitrobenzene [44]. Moreover the catalytic application of Mn_3O_4 has been extended to the combustion of organic compounds at temperatures of the range 373-773 K [45]. Polymorphs of Mn_2O_3 have been used as catalysts for removing carbon monoxide and nitrogen oxide from waste gas [46]. Mn_2O_3 is used as an electrode material for rechargeable lithium batteries [47].

1.9 Aim of the Project

According to literature survey metal oxides constitute an important class of compounds as they possess properties suitable for catalyst, superconductor, adsorbent, sensor and electrodes. There are various uses of manganese oxides as electrode material, catalyst, electrochromic material, depolarizer in dry cells, pigment for bricks, oxidizing agents, additives to feed and fertilizers and also in production of magnets etc. Several applications of manganese oxides have been stated in section 1.5. In view of the the above, it is proposed to study more about the oxides of manganese. Special emphasis will be given to study their magnetization, XRD, SEM and TGA patterns.

The proposed work will be carried out systematically in the following sequence :

(1.) Synthesis of the oxides of manganese by precipitation method.

(2.) Characterization of the above synthesized oxides .

2 EXPERIMENTAL

2.1 Materials Used

Table 4: The materials used for carrying out experiments

S.No.	Compounds	Marketed by	Grade
1	Manganese Nitrate	Lancaster	LR
2	Chromium Nitrate	MERCK	LR
3	Sodium Hydroxide	RANKEM	LR

All the chemicals used in this synthesis were used as received without further purification.

2.2 Equipments Used

Characterization and structural elucidation of the synthesized oxides were performed using techniques like Powder X-ray diffraction , Thermogravimertic analysis (TGA) , Magnetic susceptibility measurement using SQUID and Scanning electron microscopy (SEM) .

2.2.1 Thermo Gravimetric Analysis - Differential Thermal Analysis :

The TGA/DTA curves were recorded on a Perkin Elmer (Pyris Diamond) TGA-DTA High Temperature 115 instrument at Institute Instrumentation Centre (IIC), IIT Roorkee under the following conditions :

Heating Rate	------	10°C / minute
Atmosphere	------	Air
Chart Speed	------	10 cm/hour
Flow Rate	------	200 mL/minute
Reference	------	Alumina powder

Weight of reference ------ 10 mg
Weight of sample ------ 8-12 mg

2.2.2 Powder X-Ray Diffraction

These studies were carried out on Bruker D8 Advance X-Ray Diffractometer, at Institute Instrumentation Centre (IIC) , IIT Roorkee under the following conditions :

Target ------ Copper ($\lambda = 1.5418\ A^{o}$)
Filter ------ Nickel
Scanning ------ $5^{o} - 90^{o}$
Current ------ 20 mA
Range ------ 2 KC/S
Voltage ------ 35 KV
Chart Speed ------ 1 cm/minute
G.M. Speed ------ 2^{o}/minute

The peak locations were compared with X-ray indexing data cards for phase identification. X-Ray indexing cards were obtained from the Departmental Library of Metallurgy and Materials Engineering Department , IIT Roorkee.

The mean crystallite size was calculated from the XRD pattern using Debye-Scherrer equation [48].

Debye-Scherrer Formula is $D = 0.9\lambda / \beta \cos\theta$

Where, λ = X-ray wavelength ($1.5418\ A^{0}$)

β = Full width at half maxima (FWHM in Radians)

θ = Bragg's angle

D = Mean crystallite size (A^{0})

2.2.3 Field Emission-Scanning Electron Microscopy (FE-SEM)

To observe the morphology and particle size FE-SEM analysis were made. The instrument used for conducting FE-SEM was QUANTA 200 FEG made by NEI Netherlands. High voltage (20 kV) electron beam was produced by using Field Emission

Gun (FEG). The detector used for identifying back scattered electron beam was Secondary Electron Detector (SED). EDAX was used for semi quantitative analysis. The detector used for EDAX was Si-Li detector (X-ray detector). This equipment was available at Institute Instrumentation Centre (IIC), IIT Roorkee.

2.2.4 SQUID

The magnetic studies were carried out using SQUID (Superconducting Quantum Interference Device). It was Quantum Design MPMS XL model available at Institute Instrumentation Centre (IIC), IIT Roorkee. The conditions used were as follows :

Field	------	5000 gauss
Temperature	------	20 K – 150 K

2.3 Synthesis of Chromium Oxide

The synthesis of chromium oxide was carried out using Precipitation method The chromium oxide was synthesized by mixing 500 mL of 0.1 M chromium nitrate solution and 500 mL of 0.1 M sodium hydroxide solution. The chromium nitrate solution was kept in a 2000 mL beaker and the sodium hydroxide solution was taken in a separating funnel. The separating funnel was clamped on to a stand and the beaker containing chromium nitrate was placed below it on a magnetic stirrer. The sodium hydroxide solution was added dropwise to the chromium nitrate solution with a rate of around 1 drop/ seconds. pH measurements were carried out during the reaction and finally reaction was stopped when pH reached 10-12.The two were mixed slowly and stirred overnight on the magnetic stirrer at room temperature. The resulting precipitate was allowed to settle down and then was filtered on a Buchner funnel and washed several times with distilled water. The precipitate was dried overnight in an oven at 60°C. Then these were calcined. The dried product was sieved through a standard mesh size sieve.

These precipitate was then calcinated under different atmospheres as given below to obtain various forms of chromium oxides :

Atmosphere	**Temperature**	**Duration**	**Heating rate**	**Cooling rate**
Air	450°C	6 hours	50°C/hour	25°C/hour
H_2	500°C	8 hours	50°C/hour	25°C/hour
N_2	500°C	8 hours	50°C/hour	25°C/hour

A flow chart detailing the synthesis of chromium oxides is shown below:

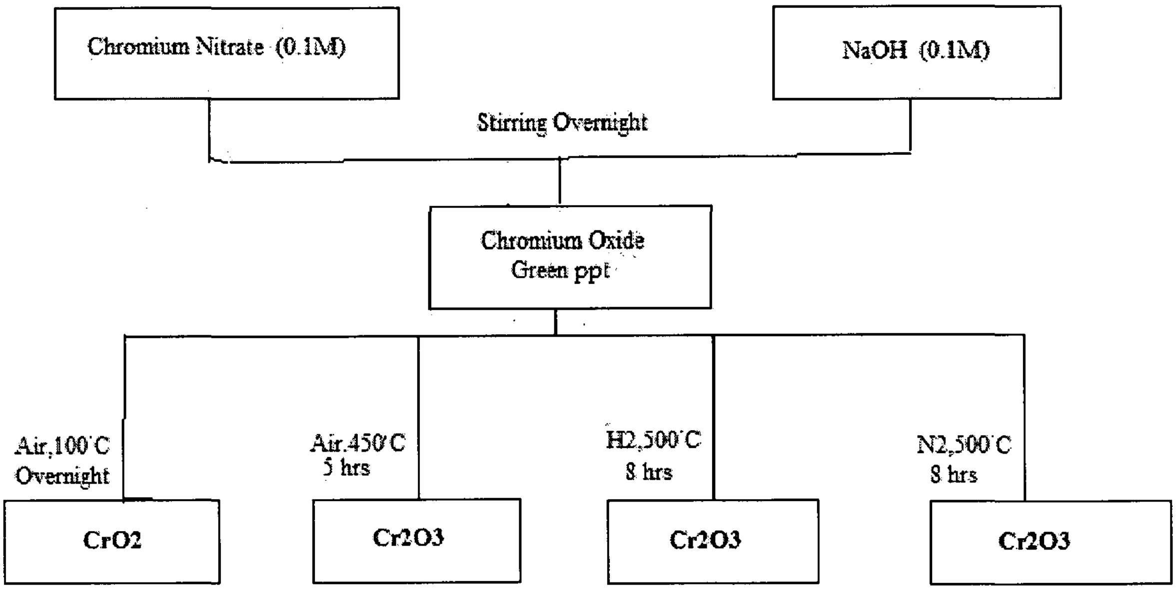

Figure1: Synthesis of Various Chromium Oxides

2.4 Synthesis of Manganese Oxide

The synthesis of manganese oxide was carried out using Precipitation method [48]. The manganese oxide was synthesized by mixing 500 mL of 0.1 M manganese nitrate solution and 500 mL of 0.1 M sodium hydroxide solution. The manganese nitrate solution was kept in a 2000 mL beaker and the sodium hydroxide solution was taken in a separating funnel. The separating funnel was clamped on to a stand and the beaker containing manganese nitrate was placed below it on a magnetic stirrer. The sodium hydroxide solution was added dropwise to the manganese nitrate solution with a rate of around 1 drop/seconds. The two were mixed slowly and stirred overnight on the magnetic stirrer at room temperature. pH measurements were carried out during the reaction and finally reaction was stopped when pH reached 10-12. The resulting precipitate was allowed to settle down and then was filtered and washed several times with distilled water using centrifuge machine. The precipitate (manganese hydroxide) was dried overnight in an oven at 60°C. Then these were calcined. The dried product was sieved through a standard mesh size sieve. Different samples of manganese oxide were prepared by calcination at different temperature ranging from 70°C to 700°C. This was done because crystallinity and other properties of manganese oxide changes with calcinations temperature.

The precursor, manganese hydroxide, was then calcinated under different atmospheres as given below to obtain various forms of manganese oxides :

Atmosphere	Temperature	Duration	Heating rate	Cooling rate
Air	300°C	5 hours	50°C/hour	25°C/hour
Air	600°C	5 hours	50°C/hour	25°C/hour
Air	750°C	5 hours	50°C/hour	25°C/hour
H_2	500°C	8 hours	50°C/hour	25°C/hour

N_2	500°C	8 hours	50°C/hour	25°C/hour

A flow chart detailing the synthesis of manganese oxides is shown below:

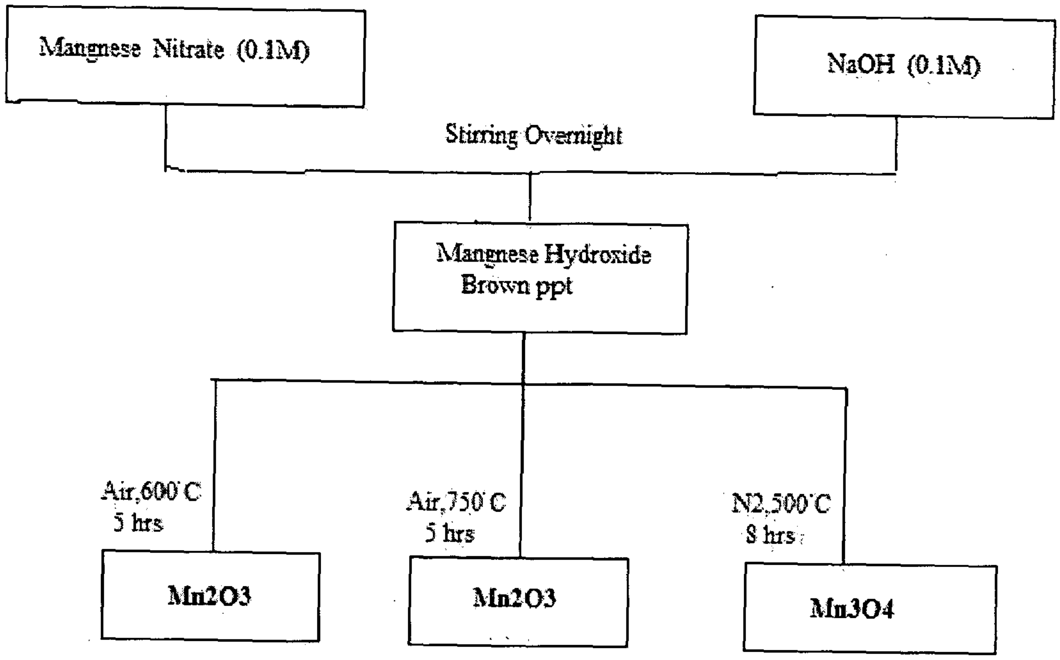

Figure 2: Synthesis of Various Manganese Oxides

3 RESULT AND DISCUSSION

Chromium and manganese oxides prepared were characterized using different techniques as given below :

3.1 Thermo Gravimetric Analysis (TGA) - Differential Thermal Analysis (DTA)

TGA was used to determine the temperature required to obtain the metal oxide from the precursor. The TGA data showed that the green powder prepared from chromium salt decomposes at ~235^{0}C. So the green product was subjected to calcinations at 450^{0}C for 5 hours in a muffle furnace. Black powder was obtained.

From the TG-DTA pattern of manganese oxide precursor it can be noticed that the different forms exist at different temperature. So the precursor was calcinated at various temperatures ~ 300, 600, 750^{0}C. It also show a small amount of water loss at 100^{0}C. At The TG-DTA curve is shown in Figure [3-5].

3.2 Powder X-Ray Diffraction

X-ray diffraction pattern is unique for each crystalline substance . With specified d-values and the relative peak intensities. It is studied by comparing the XRD pattern with the JCPDS data.

The X-Ray diffraction pattern for chromium and manganese oxides obtained upon calcinations under different atmospheres are shown in the Figures [6-12] respectively. The X-ray diffraction data for each of these are given in Tables [5-10] respectively.

The X-ray diffraction patterns indicate that the chromium oxide formed is (tetrahedral) CrO_2 with the cell parameter as: a = 4.419, c = 2.915 and three strongest lines are 3.12, 2.43, 1.64.

The oxide formed due to calcination at 450°C in air is (rhombic) Cr_2O_3. The cell parameters for this are a = 4.914, c = 13.66 and three strongest lines are 1.67, 2.67, 2.47.

The oxide formed due to calcination at 500°C in H_2 for 8 hours is Cr_2O_3 (rhombic) with the cell parameters as a = 4.954, c = 13.66 and three strongest lines are 1.67, 2.67, 2.47.

The oxide formed due to calcination at 500°C in N_2 is Cr_2O_3 (rhombic) with the cell parameters as a = 4.917, c = 13.69 and three strongest lines are 1.67, 1.43, 2.66.

The XRD of manganese oxide formed due to calcination at 600°C in air is (tetrahedral) γ-Mn_2O_3. The cell parameters for this are: a = 8.1, c = 9.4.

The oxide formed due to calcination at 750°C in air for 5 hours is Mn_2O_3 (monoclinic) with the cell parameters as a = 8.86, b = 5.24, c = 13.66, β = 90.0 and three strongest lines are 2.70, 1.66, 1.42.

The oxide formed due to calcinations at 500°C in N_2 is Mn_3O_4 (tetrahedral) with the cell parameters as a = 5.75, c = 9.42 and three strongest lines are 2.48, 2.75, 1.57.

Table 5: XRD data of chromium Oxide precursor

S.No.	**d- value (A°) Experimental**	**d- value (A°) Literature**	**I/I_0 x 100 Experimental**	**I/I_0 x 100 Literature**
1	3.1069	3.124	100	100
2	2.429	2.433	59	50
3	1.714	1.695	35	43
4	1.474	1.478	18	12
5	1.404	1.414	20	14

Table 6: XRD data for Chromium Oxide formed by calcinating at 450^0C in air and 500^0 in H_2

S.No.	d- value (A^0) Experimental	d- value (A^0) Literature	I/I_0 x 100 Experimental	I/I_0 x 100 Literature
1	3.632	3.620	50	45
2	2.664	2.670	70	70
3	2.476	2.470	79	70
4	2.172	2.170	32	30
5	1.813	1.810	30	45
6	1.670	1.670	100	100
7	1.469	1.470	31	30
8	1.429	1.430	48	45

Table 7: XRD data of Chromium oxide formed due to calcination at 500^0C in N_2

S.No.	d- value (A°) Experimental	d- value (A°) Literature	I/I_o x 100 Experimental	I/I_o x 100 Literature
1	3.620	3.629	78	74
2	2.660	2.664	100	100
3	2.476	2.478	95	91
4	2.172	2.174	40	27
5	1.813	1.814	43	35
6	1.670	1.672	86	80
7	1.462	1.464	21	26
8	1.430	1.430	40	33
9	1.294	1.295	29	12

Table 8: XRD data of manganese oxide formed by calcinating at 600^{0}C in air

S.No.	d- value (A^o) Experimental	d- value (A^o) Literature	I/I_o x 100 Experimental	I/I_o x 100 Literature
1	3.092	3.080	62	60
2	2.757	2.740	68	70
3	2.489	2.480	100	100
4	2.352	2.390	47	40
5	2.034	2.030	24	20
6	1.956	1.890	22	30
7	1.757	1.790	16	20
8	1.539	1.540	41	30

Table 9: XRD data of manganese oxide heated at 750^{0}C in air

S.No.	d- value (A^0) Experimental	d- value (A^0) Literature	I/I$_o$ x 100 Experimental	I/I$_o$ x 100 Literature
1	3.830	3.800	47	60
2	2.713	2.700	100	100
3	2.481	2.500	52	40
4	2.351	2.340	65	60
5	2.000	2.000	48	60
6	1.796	1.840	52	60
7	1.662	1.660	78	80
8	1.542	1.530	44	40
9	1.491	1.490	33	50
10	1.450	1.450	40	60
11	1.418	1.420	62	70
12	1.386	1.390	35	40
13	1.276	1.280	49	50
14	1.196	1.180	31	40

Table 10: XRD data of manganese oxide heated at 500^{0}C in N_2

S.No.	d- value (A^o) Experimental	d- value (A^o) Literature	I/I_o x 100 Experimental	I/I_o x 100 Literature
1	4.900	4.920	30	20
2	3.074	3.080	42	31
3	2.750	2.750	78	63
4	2.484	2.480	100	100
5	2.342	2.360	20	13
6	2.038	2.030	30	15
7	1.788	1.790	22	18
8	1.576	1.570	42	50
9	1.440	1.440	24	18
10	1.276	1.280	15	13

The mean crystallite size was calculated by Debye-Scherrer equation from the FWHM of the peak with 100% intensity. The calculated crystallite sizes are tabulated below.

Table 11: Crystallite sizes as calculated by Debye-Scherrer equation.

S.No	Sample	FWHM (β) (degree)	FWHM (β) (radians)	Crystallite size D (nm)
1	CrO_2	0.2	0.0039	45
2	Cr_2O_3	0.3	0.0052	46
3	Cr_2O_3	0.35	0.0061	27
4	Mn_3O_4	0.3	0.0052	33
5	Mn_2O_3	0.25	0.0044	37

3.3 FE-SEM images and EDAX data

The FE-SEM images were recorded for all the precursor samples and metal oxides are shown in figure [13-18]

The particles look agglomerated and the particles either show close to sphere like morphology or fibrous morphology. Although the primary crystallite size observed by XRD measurement is in the range of 35-45 nm, because of agglomeration the particles look bigger in SEM images. Along with FE-SEM analysis EDAX data were also recorded. They are shown in figure [19-24]. The EDAX elemental data is in good agreement with the theoretically predicted elemental percentages.

3.4 SQUID

The magnetic susceptibility for the samples as a function of temperature was recorded using Superconducting Quantum Interference Device (SQUID). The plots for magnetization vs. temperature (T) were plotted for each and are shown in figures [25-27].

Magnetization plot of chromium oxide precursor shown in figure [25] has been taken in the temperature range of 75 – 200K and the plot has a sharp fall after 80K and shows paramagnetic behavior. The antiferromagnetic transition could not be seen because we could not record below 20K temperature range in the instrument at IIC, Roorkee. The magnetization plot of manganese oxide precursor figure [26] also show paramagnetic behavior in this temperature range. Whereas the plot of manganese oxide heated at 750^0C figure [27] exhibit ferromagnetic behavior.

4 CONCLUSION

Nanocrystalline chromium oxides and manganese oxides were prepared through precipitation method. The precursor was calcined to get nanocrystalline oxides. The precursor and the oxide samples were characterized by powder XRD, TG-DTA, FE-SEM.

The XRD studies show that chromium oxide formed is CrO_2 which changes to Cr_2O_3 when heated to 500^0C either in H_2 or N_2 atmosphere but with different lattice parameters. The particle size, as calculated from Debye-Scherrer equation was around 46nm. Manganese hydroxide formed changes to Mn_2O_3 when heated at 750^0C in air whereas it changes to Mn_3O_4 when heated at 500^0C in N_2 atmosphere for 8 hours and were ~35nm in size. In FE-SEM images the particles look agglomerated with irregular morphology.

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```
Sample Weight:      21.9 mg          Temperature Program:                        Instrument: Perkin Elmer (Pyris Diamond)
Reference Weight:   20 mg                    Cel   Cel  Cel/min  min    s    Pan:        Alumina
Reference Name:     Alumina Powder   1*       23  1000      10     0  0.5    Atmosphere: Air (200 ml/min)
```

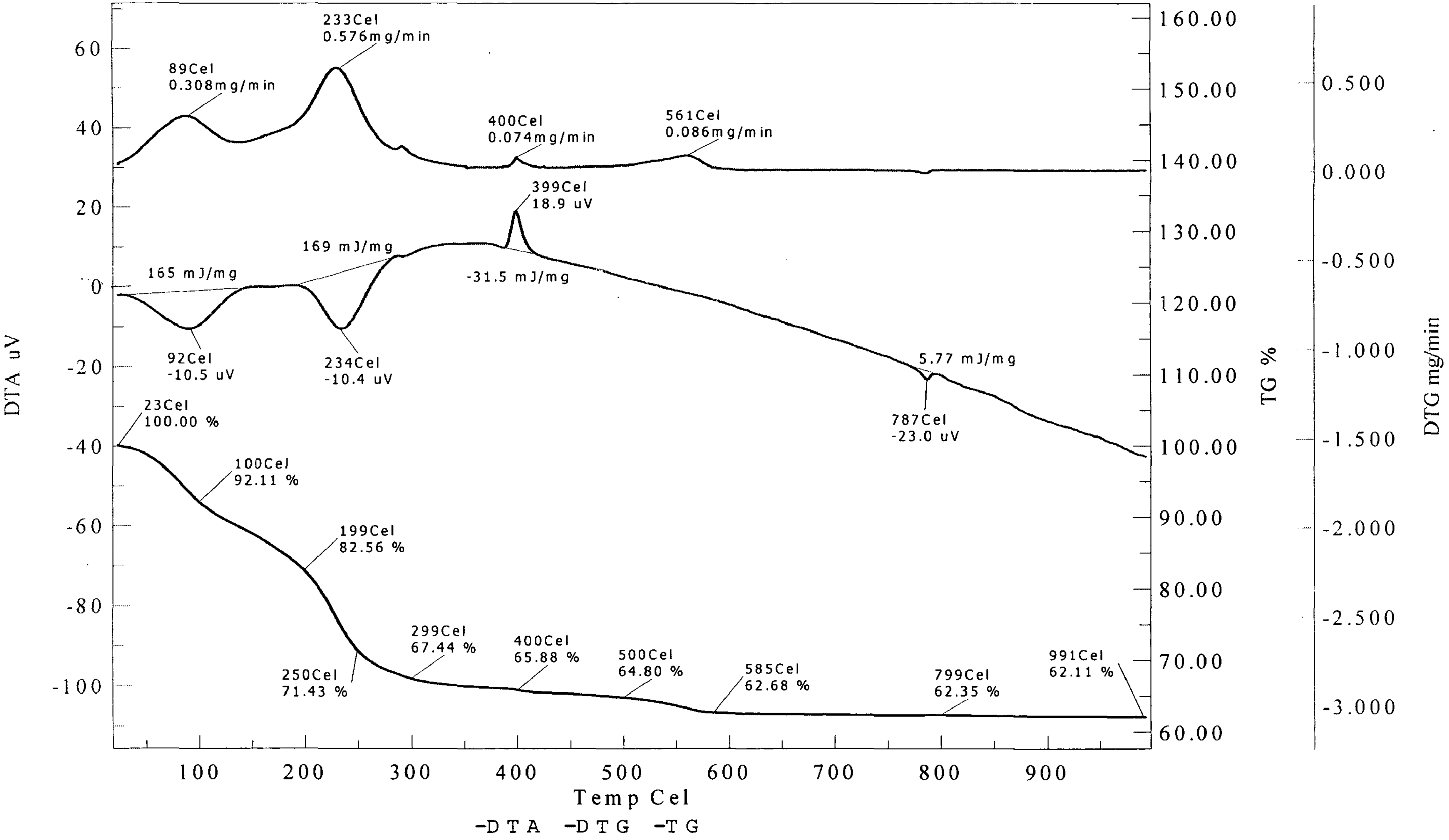

Figure 3: TG, DTG and DTA spectrum of Chromium Oxide at 10^0C/min

```
Sample Weight:     8.525 mg          Temperature Program:                      Instrument: Perkin Elmer (Pyris Diamond)
Reference Weight:  10 mg                       Cel   Cel  Cel/min  min    s  Operator:   A.K.Saini
Reference Name:    Alumina Powder    1*         25  1000       10    0  0.5  Pan:        Alumina
                                                                             Atmosphare: Air (200 ml/min)
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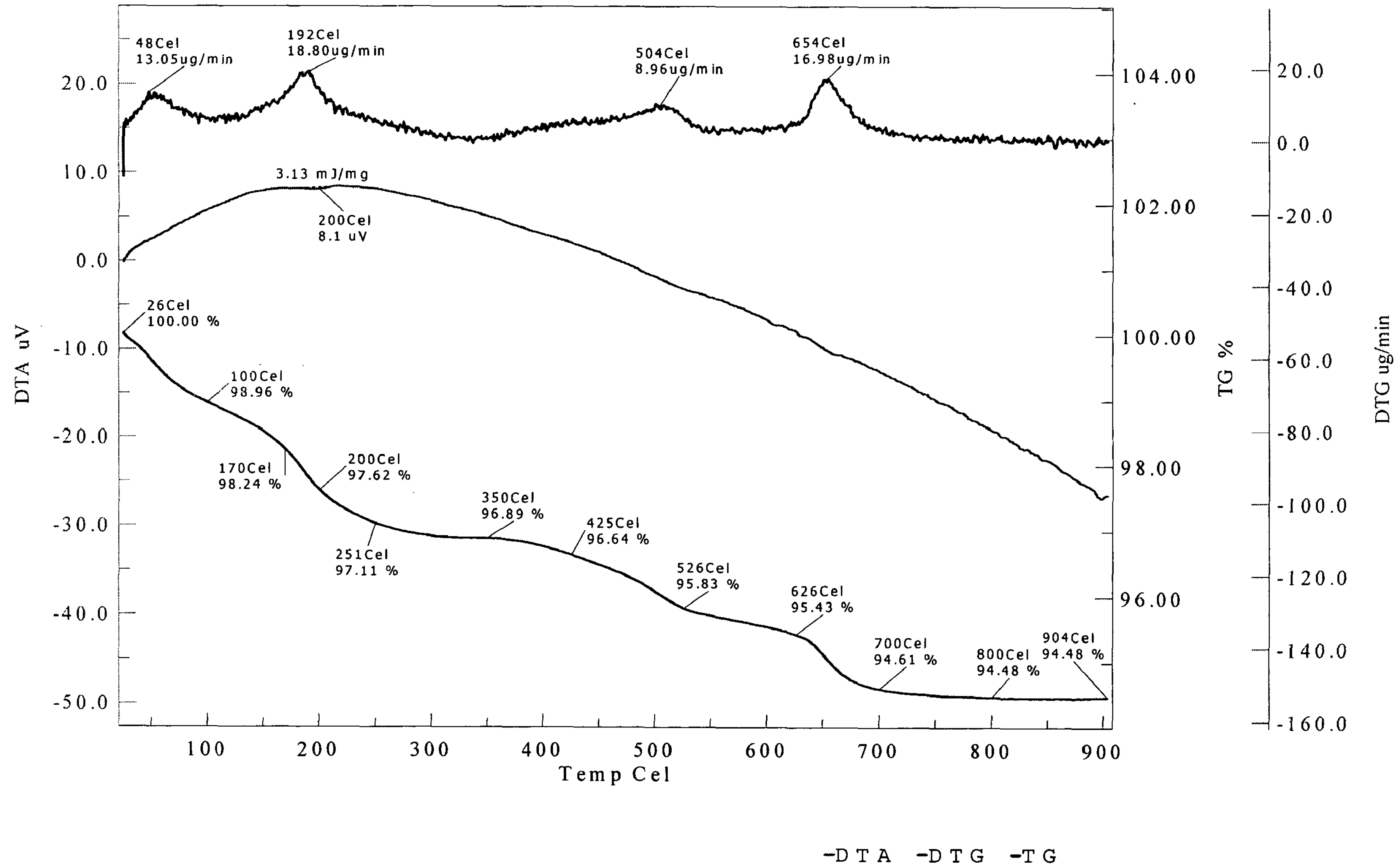
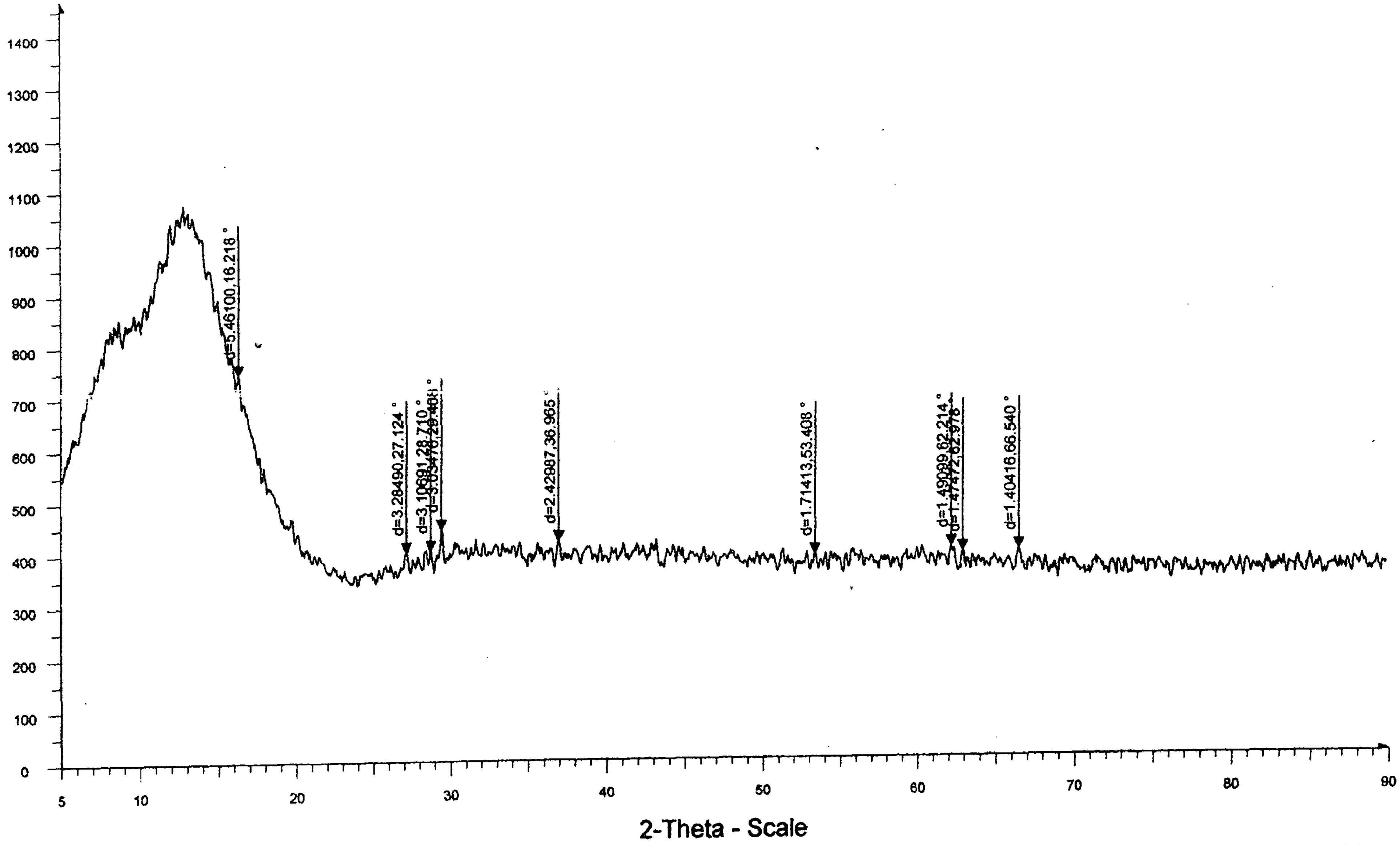
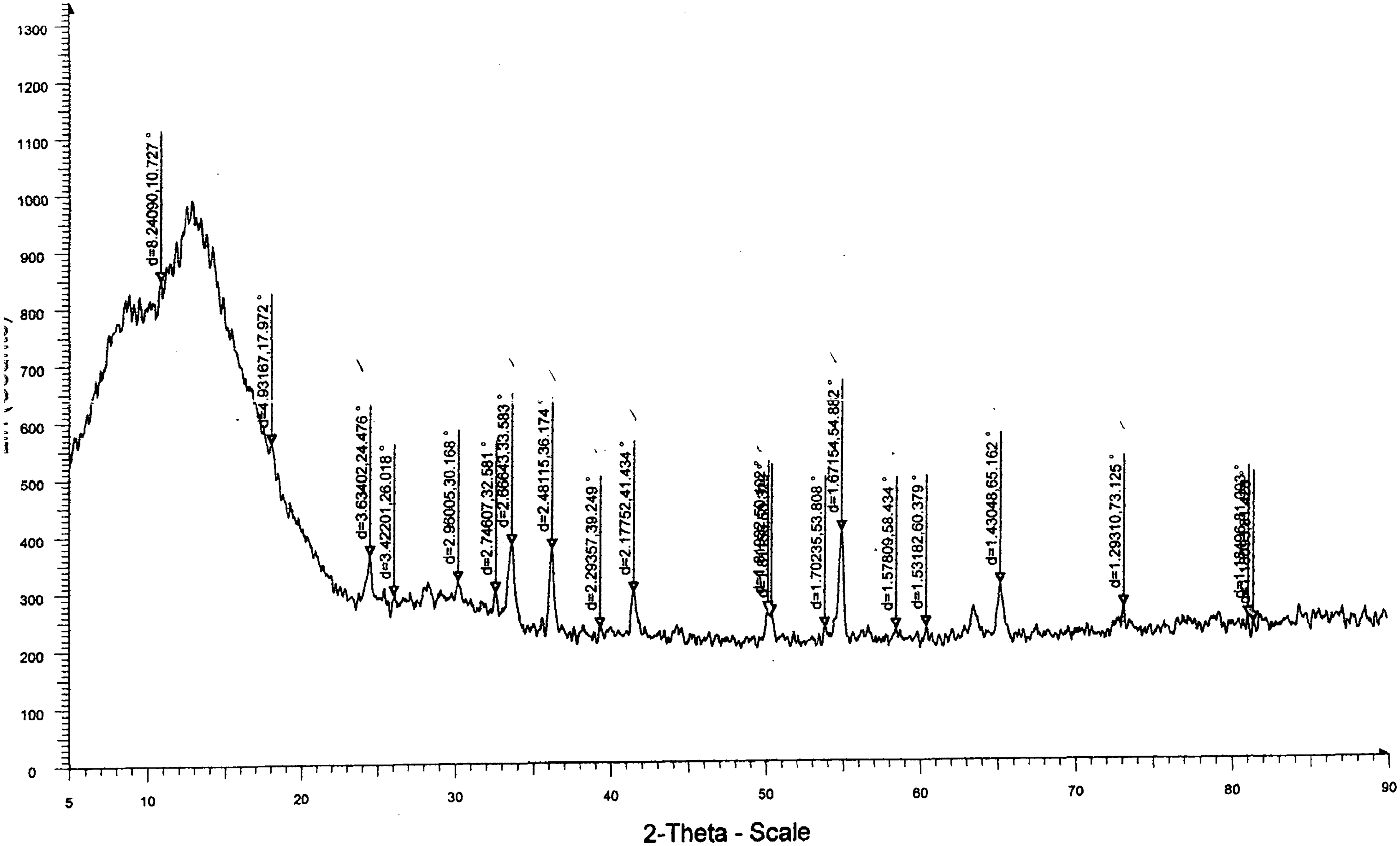


Figure 5: TG, DTA and DTG spectra of Manganese Oxide



NV-11 - File: NV-11.raw - Type: 2Th/Th locked - Start: 5.000 ° - End: 90.000 ° - Step: 0.050 ° - Step time: 3. s - Temp.: 25 °C (Room) - Time Started: 1199087232 s - 2-Theta: 5.000 ° - Theta: 2.5
Operations: Smooth 0.150 | Y Scale Mul 0.750 | Import

Figure 6: XRD spectra for chromium oxide precursor.



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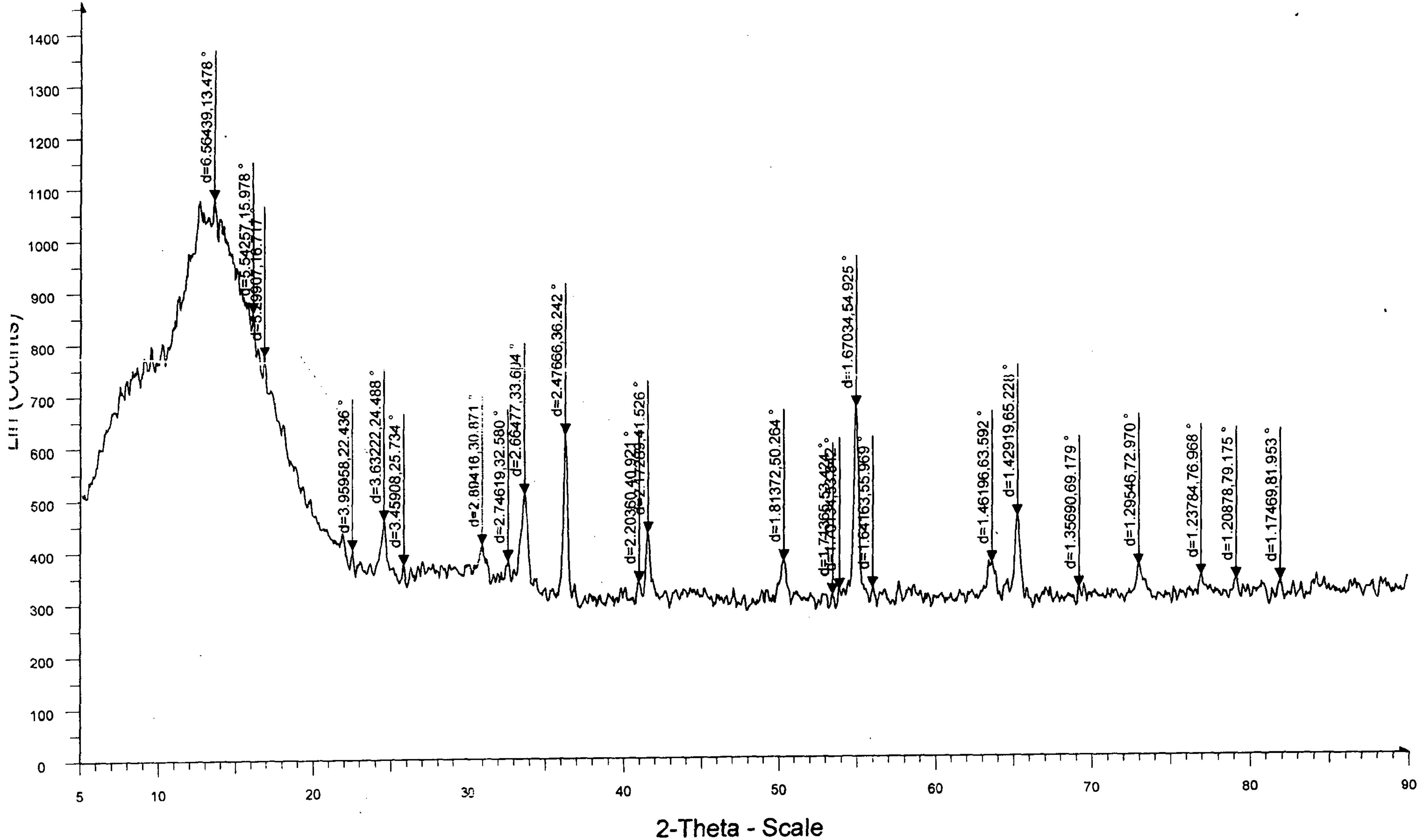
Operations: Smooth 0.150 | Y Scale Mul 0.750 | Import

Figure 7: XRD spectra for chromium oxide heated in air



(1) - File: (1).raw - Type: 2Th/Th locked - Start: 5.000 ° - End: 90.000 ° - Step: 0.050 ° - Step time: 3. s - Temp.: 25 °C (Room) - Time Started: 1212206720 s - 2-Theta: 5.000 ° - Theta: 2.500 ° - Operations: Smooth 0.150 | Y Scale Mul 0.750 | Import

Figure 8: XRD spectra for chromium oxide heated in H_2 atmosphere.

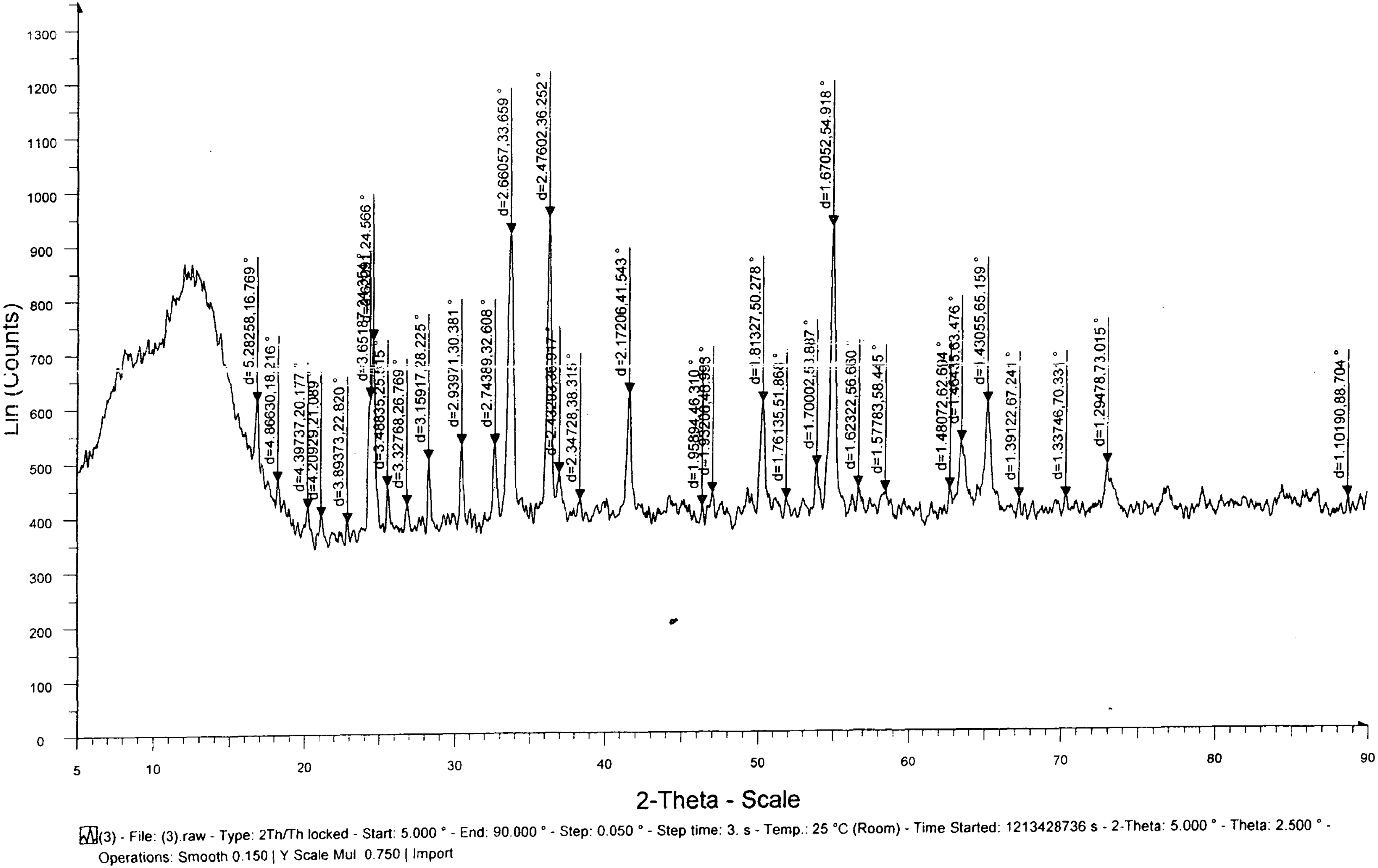


Figure 9: XRD spectrum of chromium oxide heated at 500°C in N_2.

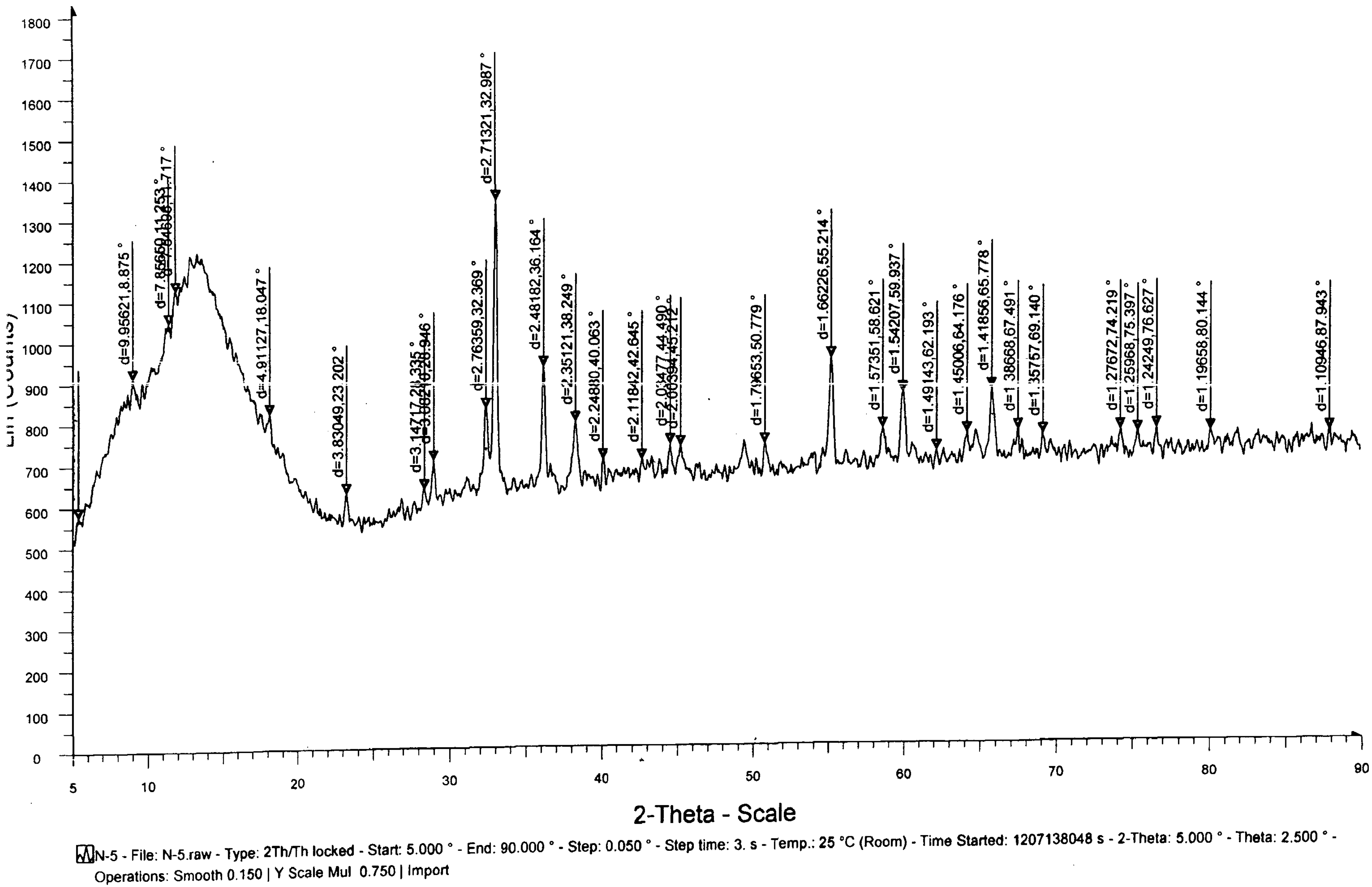


Figure 11: XRD spectrum of manganese oxide heated at 750°c in air.

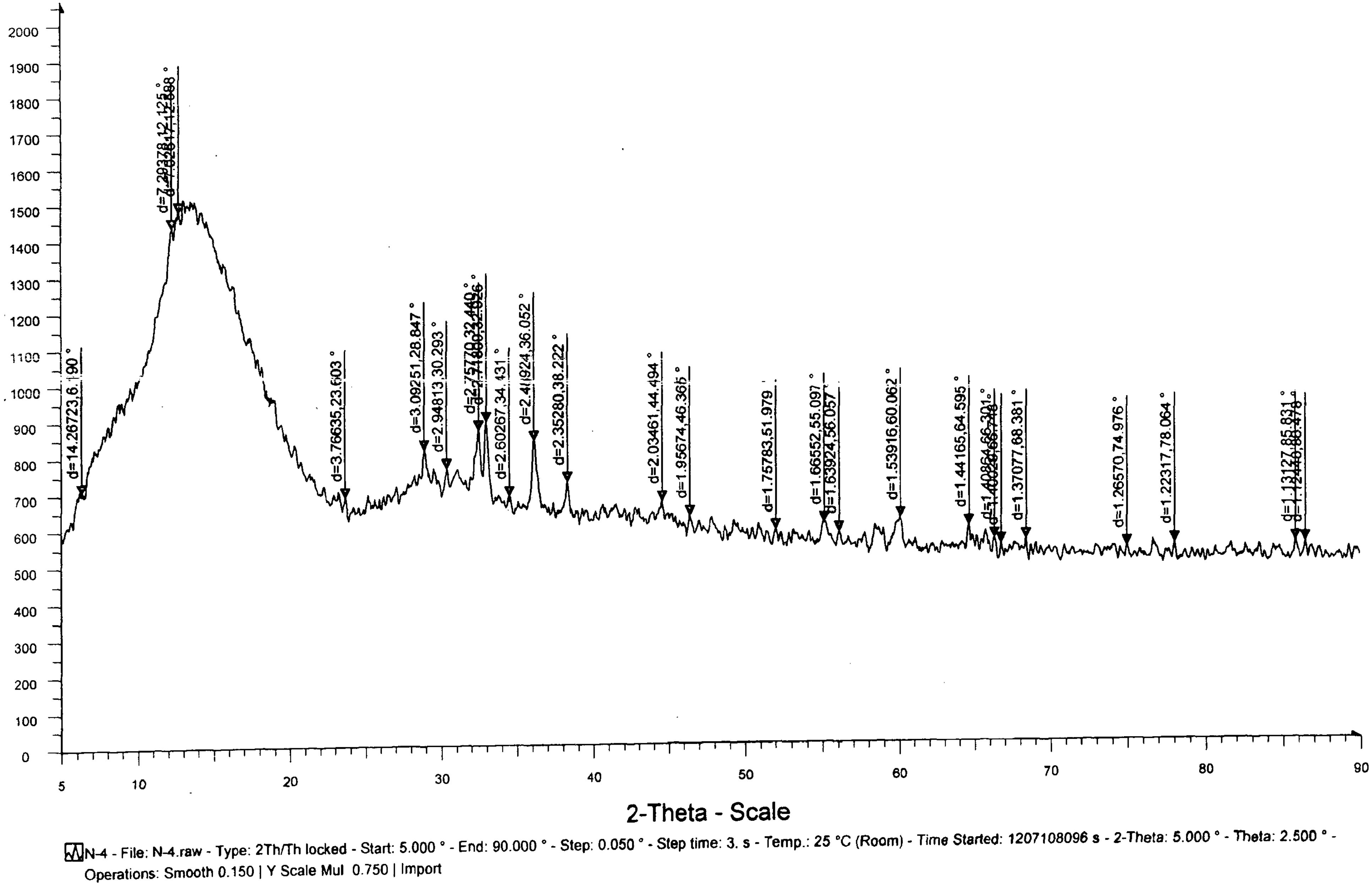


Figure 12 : XRD spectrum of manganese oxide heated at 500°c in N_2 .

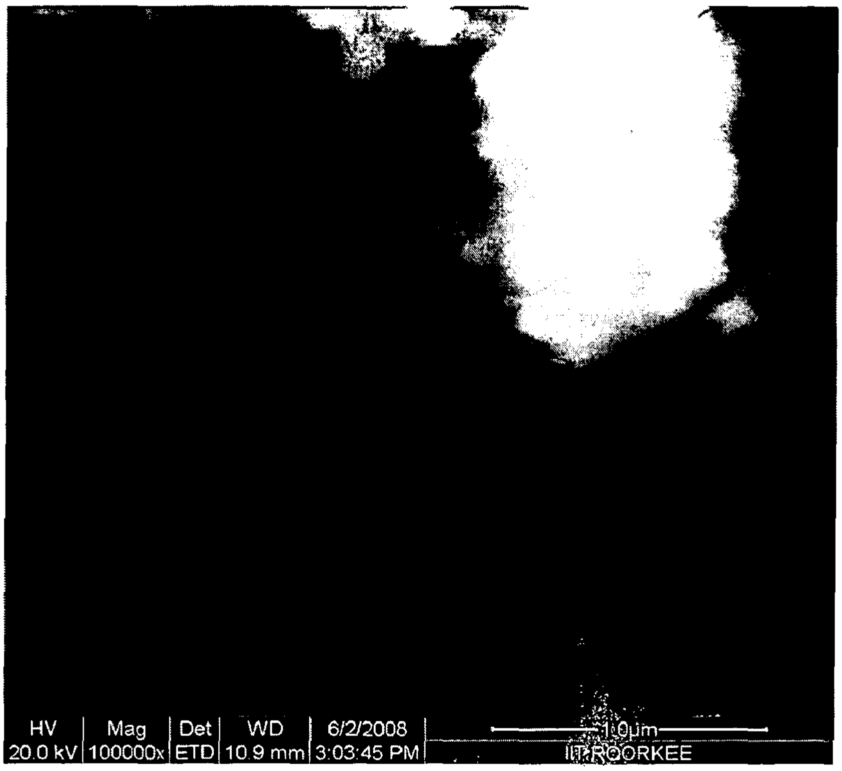


Figure 13: SEM image of chromium oxide heated at 500^0C in H_2

Figure 14: SEM image of chromium oxide heated at 500^0C in N_2

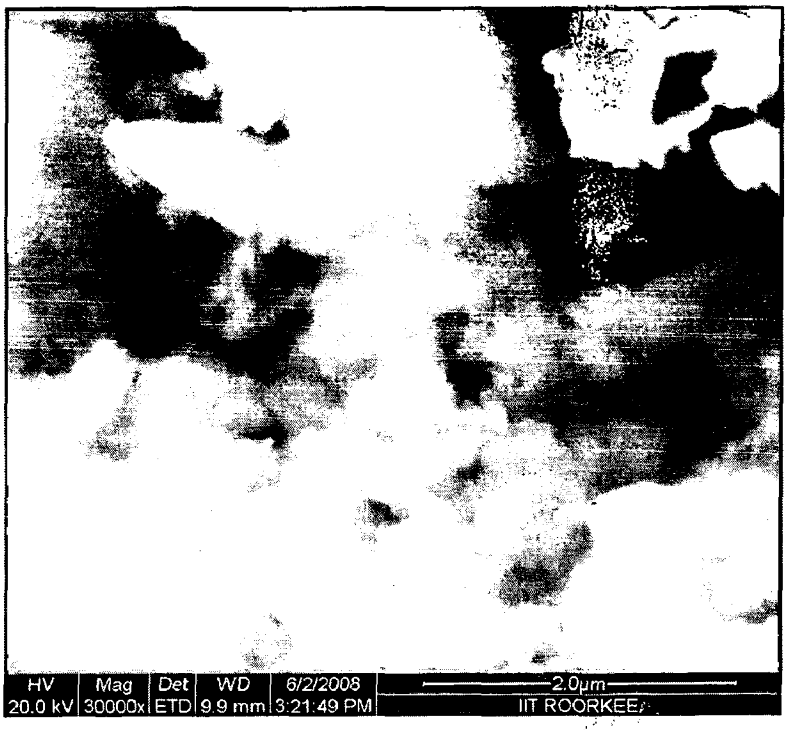


Figure 15: SEM image of manganese oxide heated at 500^{0}C in H_2

Figure 16: SEM image of manganese oxide heated at 500^{0}C in N_2

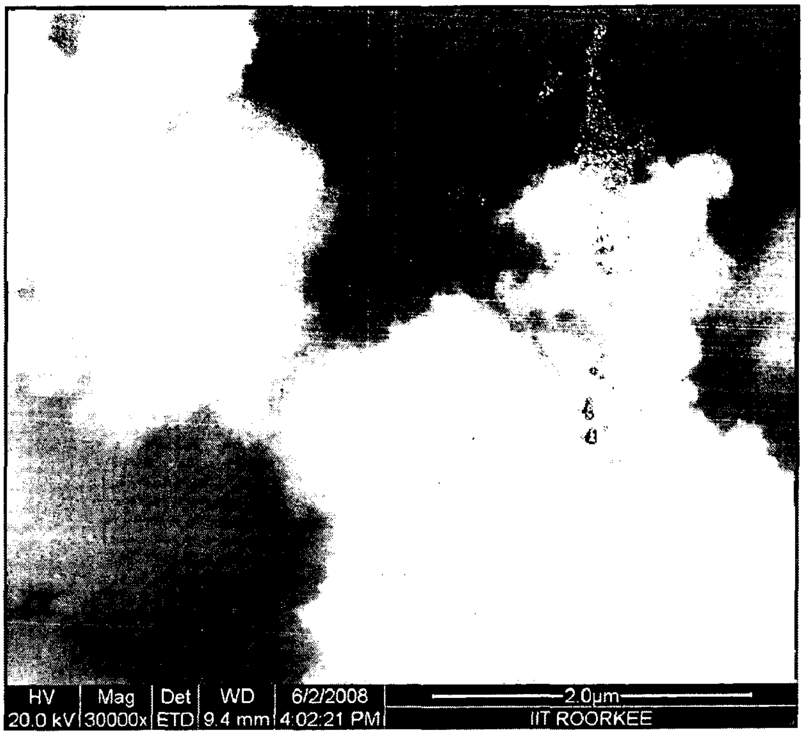


Figure 17: SEM image of manganese oxide precursor

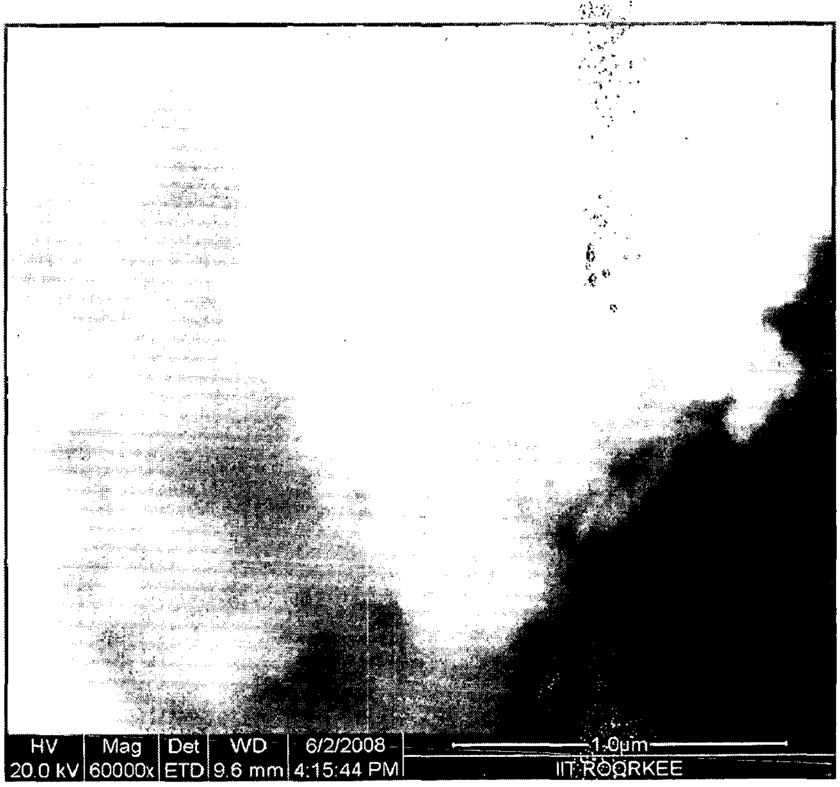
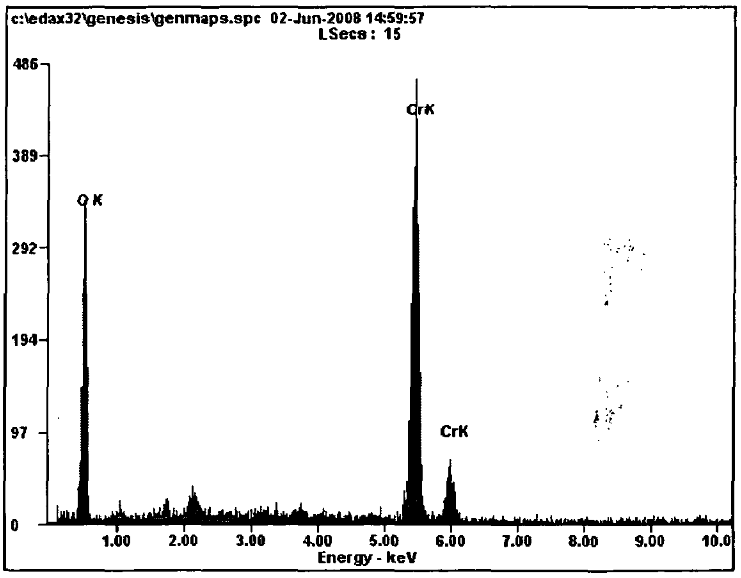


Figure 18: SEM image of manganese oxide heated at 750^0C in air



Element	***Wt%***	***At%***
OK	23.17	49.49
CrK	76.83	50.51
Matrix	Correction	ZAF

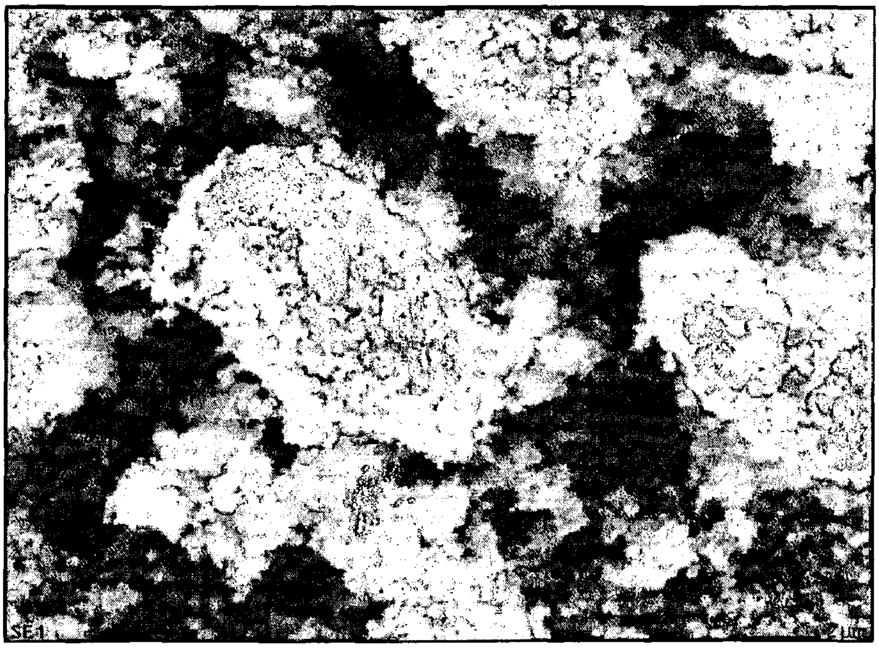
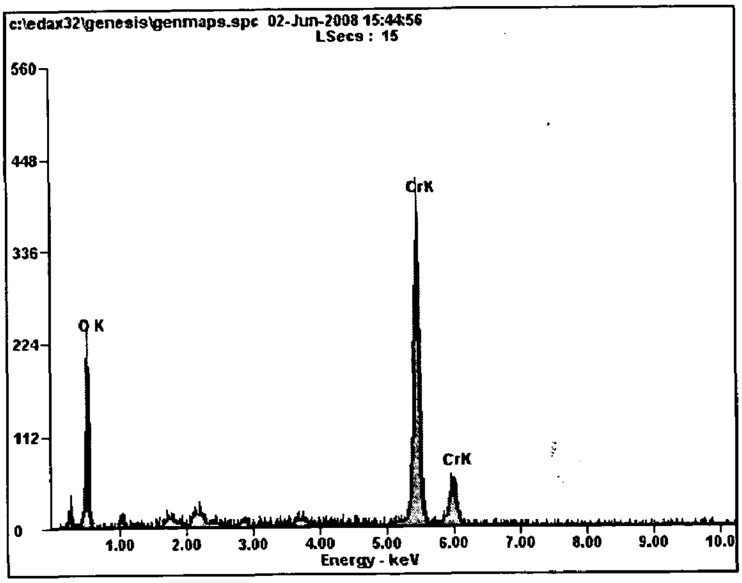


Figure 19: EDAX data of chromium oxide heated at 500^{0}C in H_2



Element	*Wt%*	*At%*
OK	20.56	45.69
CrK	79.44	54.31
Matrix	Correction	ZAF

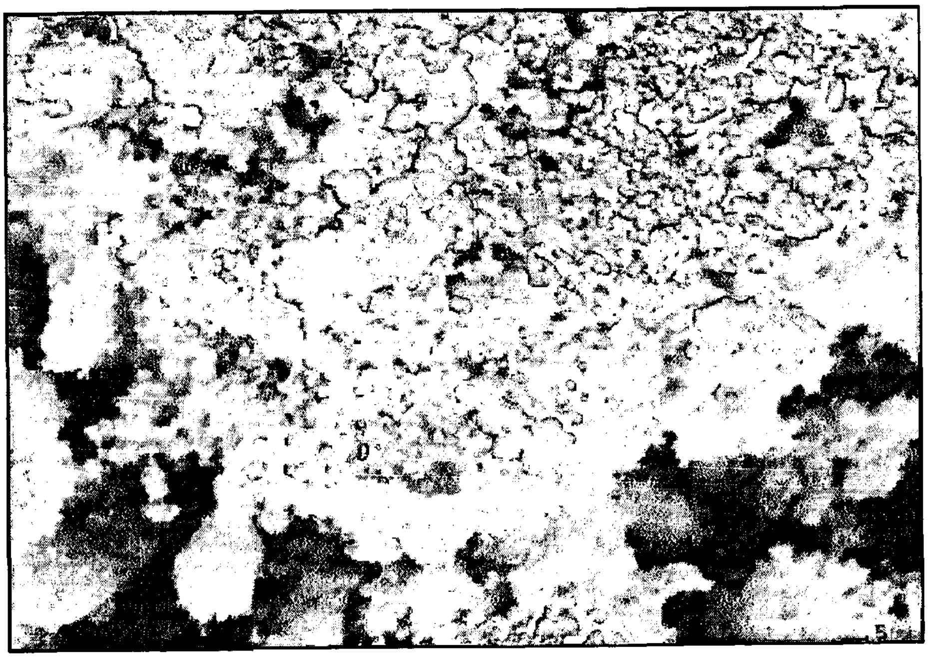
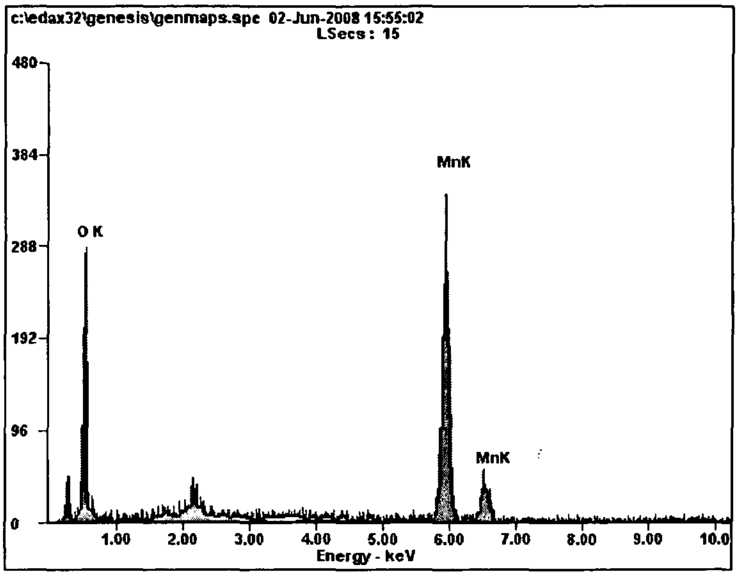


Figure 20: EDAX data of chromium oxide heated at 500^{0}C in N_2



Element	***Wt%***	***At%***
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MnK	76.50	48.67
Matrix	Correction	ZAF

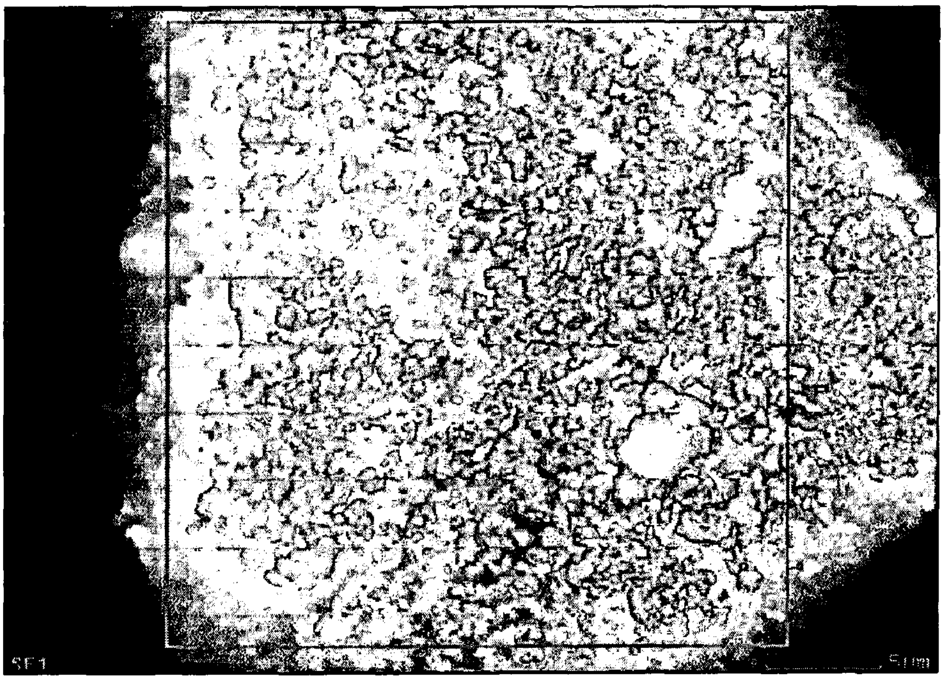
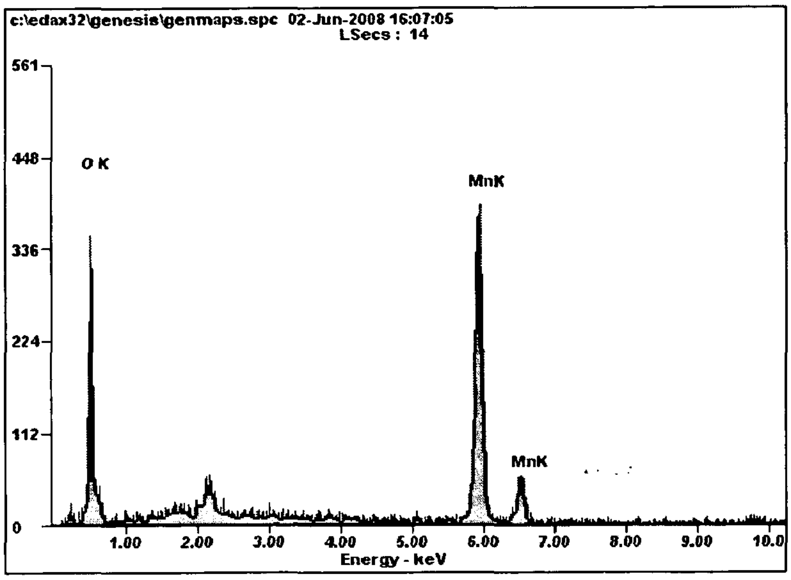


Figure 21: EDAX data of manganese oxide precursor



Element	*Wt%*	*At%*
OK	24.69	52.96
MnK	75.31	47.04
Matrix	Correction	ZAF

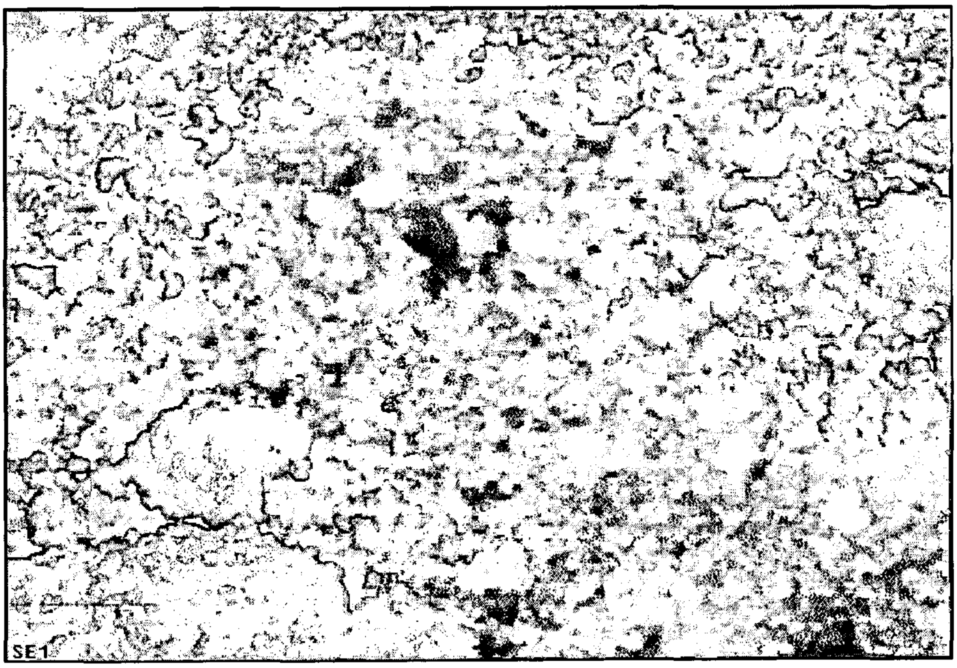
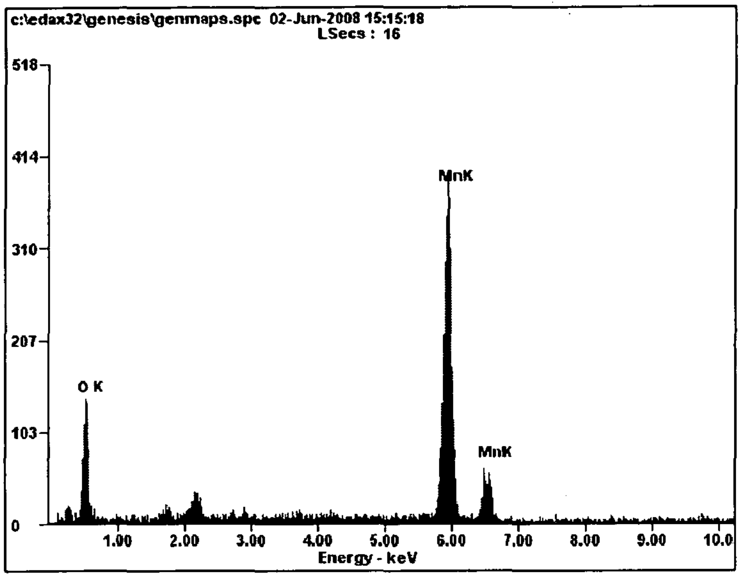


Figure 22: EDAX data of manganese oxide heated at 750^0C in air



Element	***Wt%***	***At%***
OK	12.60	33.10
MnK	87.40	66.90
Matrix	Correction	ZAF

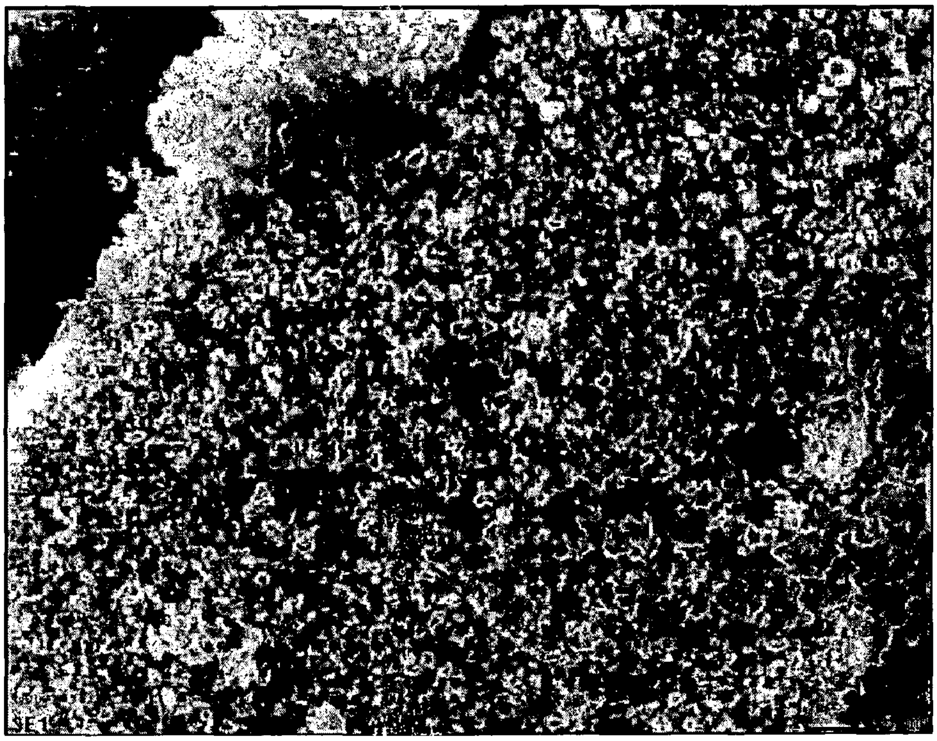
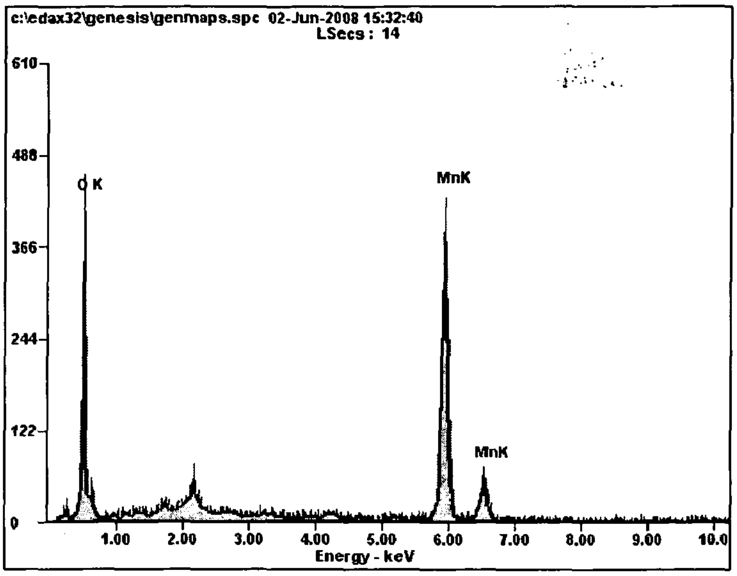


Figure 23: EDAX data of manganese oxide heated at 500^0C in H_2



Element	*Wt%*	*At%*
OK	27.54	56.62
MnK	72.46	43.38
Matrix	Correction	ZAF

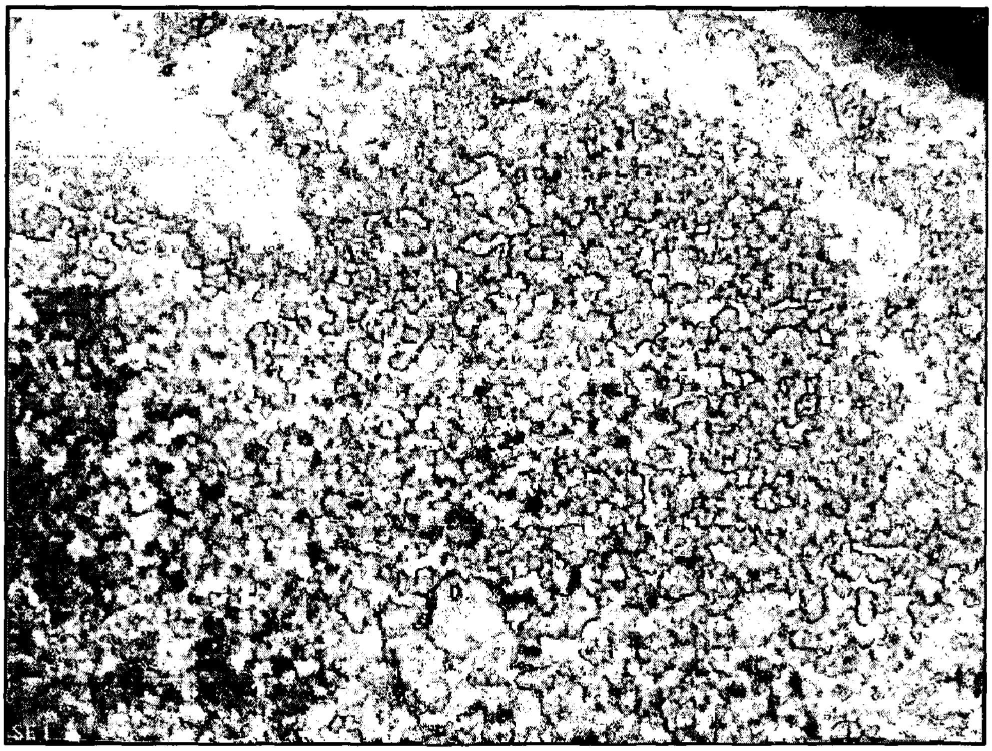


Figure 24: EDAX data of manganese oxide heated at 500^{0}C in N_2

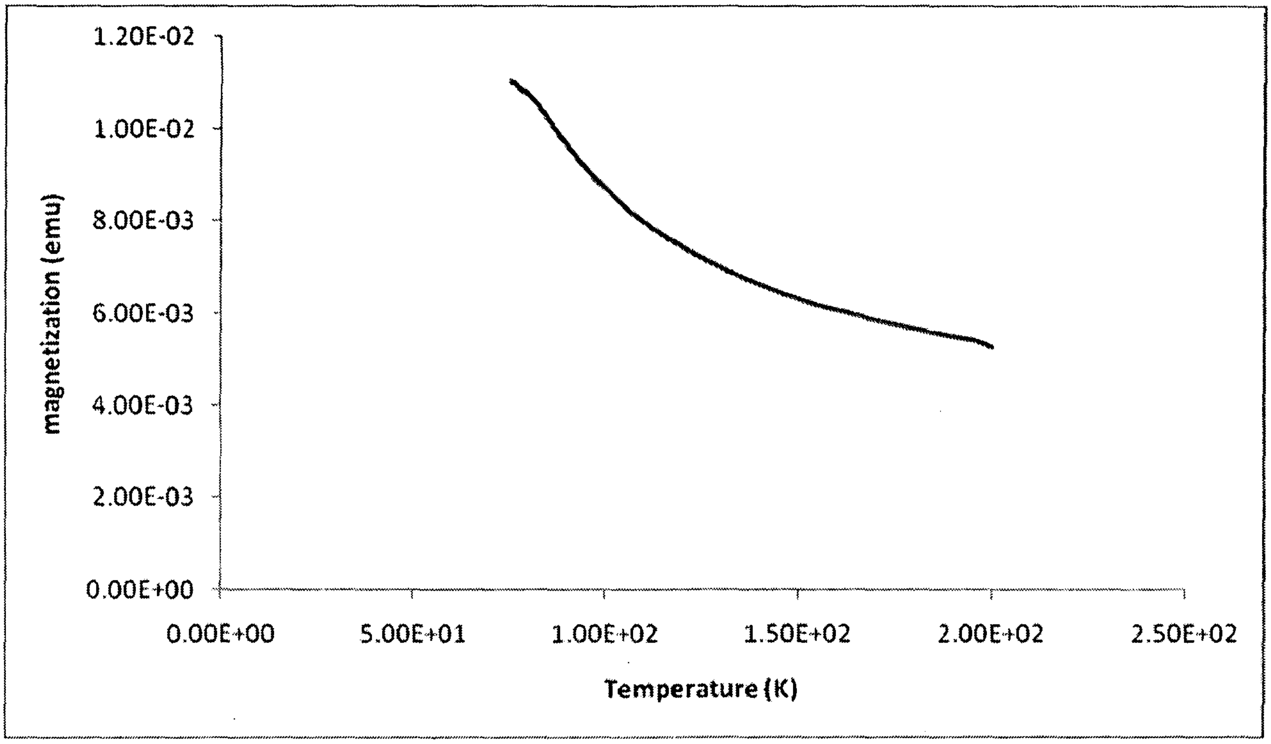


Figure 25: Magnetization Graph of CrO_2

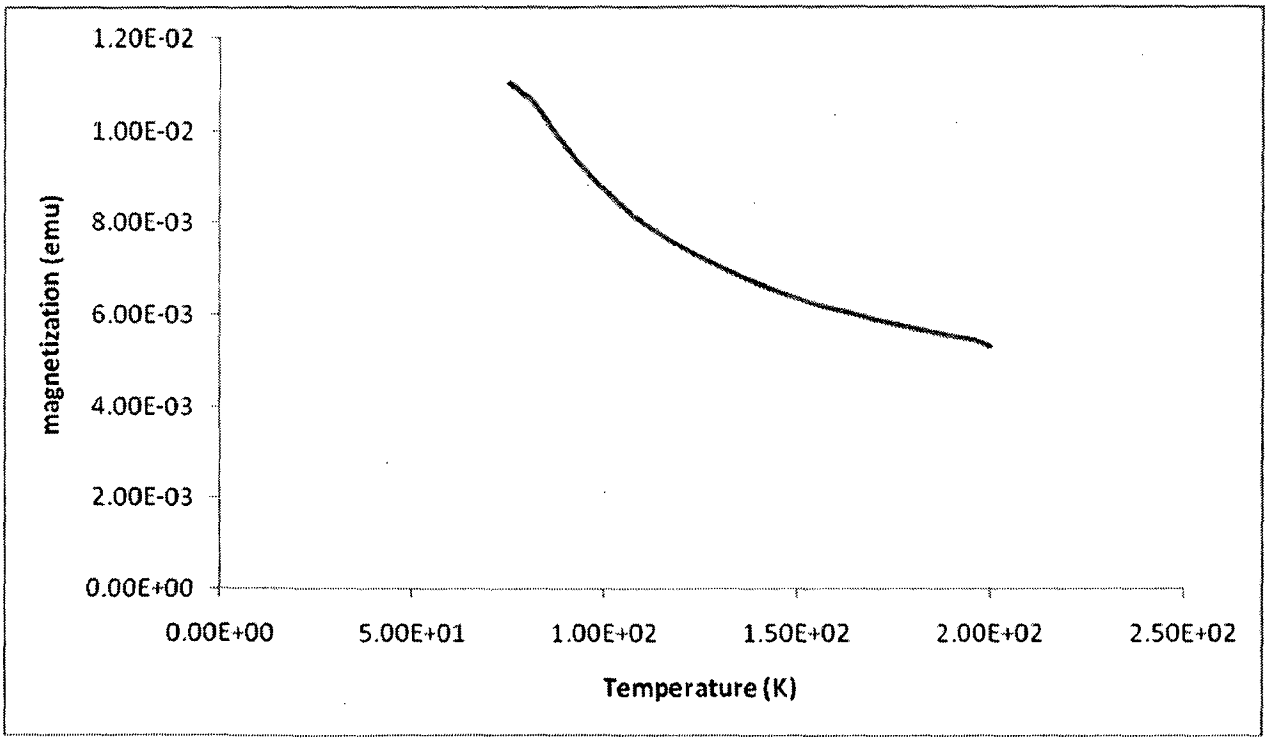


Figure 26: Magnetization Graph of Manganese Oxide precursor

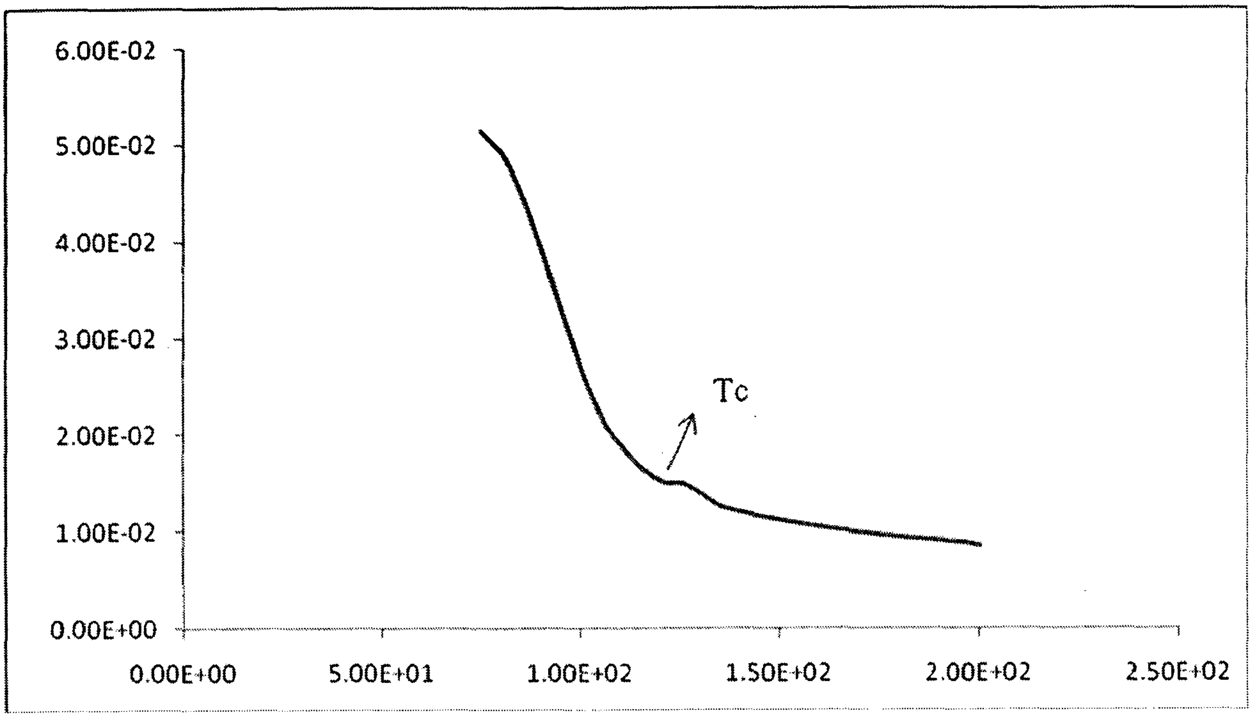


Figure 27: Magnetization Graph of Mn_2O_3