

CHAPTER-I

General Introduction.

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1.1 Thin Films :

The science and technology of thin films have been the subject of growing interest in recent years, because of their widespread applications in several fields. The increasing industrial demand for reliable thin films in microelectronic devices (thin film transistors, ICs, switching circuits, etc.) have led to tremendous advances in this field. Thin films have extensive applications in several optical devices also.

A film bounded by two parallel planes extending infinitely in two directions but is restricted in its dimensions along the third direction is called thin film. The dimensions along the third direction is called thickness of the film. The nature of distribution of material gives two types of films : (a) discontinuous films and (b) continuous films. Thin films often show anomolous behaviour compared to those of the bulk.

1.2 Types of Oxides :

From a more general point of view, oxides are of wide natural occurrence. They are grouped according to their properties as metallic oxides, semiconducting oxides, insulating oxides, superconducting oxides, magnetic oxides, etc. All of these oxides are grouped in common forms systematically as follows,

AO (Protoxides) e.g. NiO, EuO, MnO, FeO, etc.

AO₂ (Dioxides) e.g. MnO₂, PrO₂, UO₂, etc.

A₂O₃ (Sesquioxides) e.g. Ti₂O₃, V₂O₃, Co₂O₃, etc.

ABO₃ e.g. TbAlO₃, YFeO₃, YbMnO₃, LuCrO₃, etc.

AB₂O₄ (Intermediate oxides) e.g. FeFe₂O₄, CoFe₂O₄,
MnMn₂O₄, etc.

A₃B₂C₃O₁₂ e.g. Eu₃Ga₅O₁₂, Ho₃Fe₅O₁₂, Dy₃Al₅O₁₂, Gd₃Ga₅O₁₂,
etc.

1.3 Transition Metal Oxides :

In the unsaturated transition metal oxides there are always unpaired 'd' electrons associated with transition metal ions. The crystals consist of O²⁻ anions and partially ionized metallic Mⁿ⁺ cations. The band arising primarily from '2P' orbitals on the anions is completely filled at zero temperature and is well below the partially filled 'd' band arising from the 'd' orbitals of the cations. On the other hand, the band coming primarily from the 's' orbital of the cations is raised in energy well above the 'd' band as the separation between the '2P' band and 's' band is essentially the bonding - antibonding splitting that is responsible for the binding of the material. This interaction is large, of the order of 20 eV (see fig. 1.1)/1/. The 's' band is completely empty at zero temperature. The only states in the vicinity of the Fermi energy are those in the 'd' band. In transition metal oxides, the 'd' band is therefore responsible for both the electrical and the

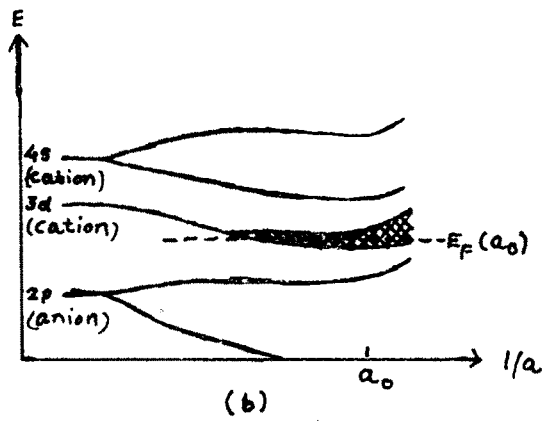
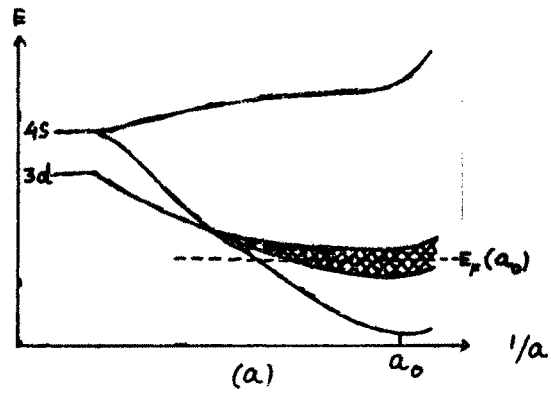


Fig. 1.1 Sketch of energy band structure as a function of inverse lattice parameter for (a) a transition metal of the iron group, and (b) an iron group transition metal oxide.

The equilibrium lattice parameter, a_0 , and the Fermi energy, E_F , at $T=0$ are indicated.

magnetic properties of material.

The transition metal oxides are interesting as the elementary Bloch-Wilson theory of electrical conductivity fails. According to this theory a material all of whose bands are either completely full or entirely empty is usually an insulator, whereas a material with a partially full band must be metallic. If the bands on both sides of the Fermi-energy actually overlap, then a crystal is an insulator according to its structure and composition but it works as a metal. The vast majority of transition metal oxides have a partially filled band but act as insulators.

The splitting of the 'd' band into states per cation by the crystalline field of the material is important in the transition metal oxides as each cation is surrounded by regular or distorted octahedron or tetrahedron of charged O^{2-} ions i.e. it is in a very strong crystalline field. The maximum limit of splitting the bands by the crystalline field is five doubly degenerate bands. Thus as long as there is only one cation per unit cell of the crystal, any material with an odd number of 'd' electron per cation must have a partially filled band according to elementary theory e.g. MnO. At room-temperature it has the (cubic) rocksalt structure, so that the '3d' band splits into a lower sixfold degenerate ' t_{2g} ' band and an upper fourfold degenerate ' e_g ' band. Spin-orbit coupling could split the ' t_{2g} ' band into fourfold and doubly degenerate bands, but, since MnO contains five '3d' electrons per unit cell, there is a

partially filled band. Thus, Bloch-Wilson theory predicts that MnO should be metallic. However, the room temperature conductivity of pure MnO is in the vicinity of $10^{-15} \Omega^{-1} \text{cm}^{-1}$

Similar analyses apply to a large number of these oxides. Band theory predicts that they should be metallic but experimentally they are highly insulating. This could be explained as in the oxides the 'd' bands are too narrow to support metallic conductivity and therefore, since no 's' and 'p' bands are present in the vicinity of the Fermi energy in these materials, they must all be nonconductors e.g. ReO_3 . This material has one '5d' electron outside of filled bands. Optically, in this material the ' σ_s ' band appears to be sufficiently above the '5d' band to be completely negligible in a discussion of electrical conductivity. Since a 'd' band cannot support metallic conductivity, ReO_3 should be an insulator. However, the room-temperature conductivity of ReO_3 approaches $10^5 \Omega^{-1} \text{cm}^{-1}$ and it is an excellent metal. A number of other oxides turn out to be good metals, with only 'd' band conductivity. There is still another class of oxides, whose members are excellent insulators at low temperatures but are metals at high temperatures.

1.4 Manganese Oxides :

The general formulae of transition metal oxides are AO , A_2O_3 , A_3O_4 , AO_2 , A_2O_5 , AO_3 , $\text{A}_n\text{O}_{2n-1}$ and $\text{A}_n\text{O}_{2n+1/2}$. The nature of bonding varies any where from ionic [e.g. NiO,

CoO] to covalent [e.g. OsO_4 , RuO_4], metallic in TiO, NbO and ReO_3 . Crystal structure of these oxides vary from cubic to triclinic symmetry. Many sesquioxides (A_2O_3) possess the corundum structure in which each A^{3+} ion is octahedrally surrounded by six O^{2-} ions and each O^{2-} ion is surrounded tetrahedrally by four A^{3+} ions. The oxides having the formula AO have a NaCl type crystal structure in which each A^{2+} is octahedrally surrounded by six O^{2-} ions and each O^{2-} ion is surrounded by six A^{2+} ions. The dioxides AO_2 have the rutile structure, while the oxides, A_3O_4 ($\text{AO} \cdot \text{A}_2\text{O}_3$) have the spinel structure.

All oxides are thermodynamically stable, as shown by their negative heats of formation. Oxides of the same metal in different oxidation states have different stabilities and therefore can be partially decomposed or disproportionated on heating. This reaction has been utilized in the preparation of intermediate oxides.

Some oxides show phase transitions from one crystal structure to another accompanied by changes in magnetic, electrical and other properties.

Many transition metal oxides show wide ranges of stoichiometry. Deviation from stoichiometry can be due to cation or anion deficiency. Large deviation due to marked change in unit cell dimensions or in crystal structure. Electrical conductivity is markedly affected by deviations from stoichiometry. Impurities cause change in the properties

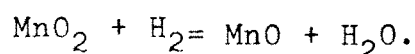
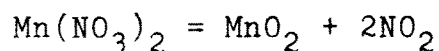
of metal oxides.

Transition metal oxides exhibit a wide range of magnetic properties. They show a spectacular range of values of electrical conductivity. Conduction in semiconducting oxides involves the hopping of charge carriers or the excitation from valence band to the conduction band.

Manganese oxides are transition metal oxides. There are six forms of it as manganosite - MnO , pyrolusite - MnO_2 , MnO_3 , Mn_2O_3 , Mn_2O_7 and hausmannite - Mn_3O_4 . Out of these six oxides MnO_3 and Mn_2O_7 are not stable. These oxides are called binary oxides. Each oxide has different stoichiometric ratio.

MnO :

This oxide is prepared by reduction of higher oxides by H_2 or CO or by pyrolysis of metal hydroxide or carbonate. Usually it is produced by heating MnO_2 in an atmosphere of hydrogen or by thermal decomposition of MnCO_3 . Manganese carbonate must be heated to $1000 - 1100^\circ\text{C}$ for 15-20 minutes to get MnO . After heating $\text{Mn}(\text{NO}_3)_2$ in air to about 300°C , MnO_2 is formed. Further MnO_2 is reduced at 800°C with pure, oxygen free hydrogen, for a long time to get $\text{MnO}/3/$.



MnO has rocksalt structure above 120°K . Below 120°K it undergoes a 0.8% rhombohedral distortion.

It is antiferromagnetic basic oxide. Pure MnO is an insulator at room-temperature. By doping with 0.1% Li , it

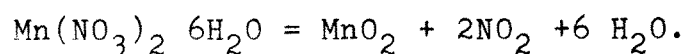
becomes semiconducting and has band gap $E_g = 1.8$ eV (Crevecocar and de Wit 1968) and $E_g = 2.2$ eV (o'Keefe and Valigi 1970) and activation energy $E_a = 0.5$ eV. It has resistivity $10^9 - 10^{15}$ Ω cm at room temperature. Below 820°K the activation energy is 0.37 eV and at high temperature it is increased to 1.4 eV. The Hall mobility is temperature independent in the range $500^\circ - 800^\circ\text{K}$. The sign of the Hall coefficient is normal. The increase in activation energy at high temperatures indicates onset of intrinsic conductivity, the energy gap is of the order of 2.8 eV. Since there is a strong phonon absorption from 0.03 - 0.1 eV, an antiferromagnetic peak is unobservable. The magnetostrictive distortion is large in MnO. In MnO there is p-type photoconductivity due to conduction of holes present due to non-stoichiometry or due to hole excitation.

It is used as an ore of manganese.

MnO₂ :

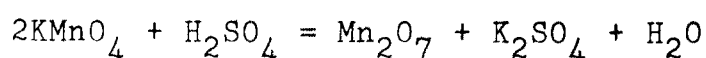
This oxide is prepared by heating $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, from MnCl_2 and $(\text{NH}_4)_2\text{S}_2\text{O}_8$, NH_4MnO_4 and NH_3 in aqueous solution and from Mn_2O_7 .

$\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is decomposed first in air by heating to about 190°C , the product in powder form is boiled with concentric nitric acid and heated in air to $450-500^\circ\text{C}$.

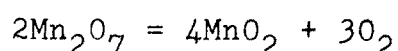


MnO_2 can be produced by electrolytic method. For this $\text{MnSO}_4/\text{H}_2\text{SO}_4$ mixture is used. The temperature of the mixture is

maintained at 70-100°C and it is efficiently controlled by a current density in the range 3-15 A/dm²/4/. On heating at 425°C for one day C-MnO₂ transforms into β-MnO₂ i.e. pyrolusite



Mn₂O₇ further decomposes.

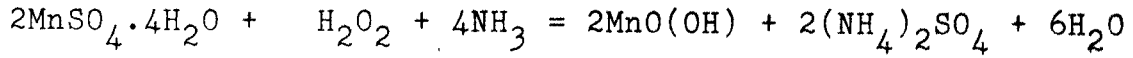


Pyrolusite has the rutile structure, the cations forming a body-centered tetragonal lattice with $c/a < 1$.

It is antiferromagnetic acidic oxide /5/. It is degenerate-semiconductor (high conductivity with little or no variation with temperature). The resistivity of polycrystalline sample is of the order of 10-1000 Ωcm, and activation energy of 0.1 - 0.3 eV/6,7/. Wiley and Knight /8/ studied unpressed crystals and found a room-temperature resistivity of only 0.1 Ωcm. The activation energy was 0.02 eV from 200° to 400°C, increasing to 0.8 eV above 400°C. This break in activation energy may signal the change from extrinsic to intrinsic conduction or may be connected with the fact that 400°k is near the ferroelectric curie temperature of MnO₂. The Hall mobility is 1.2 cm²/V-sec/9/ and the sign of R_H and thermoelectric power indicate n-type conductivity dominates.

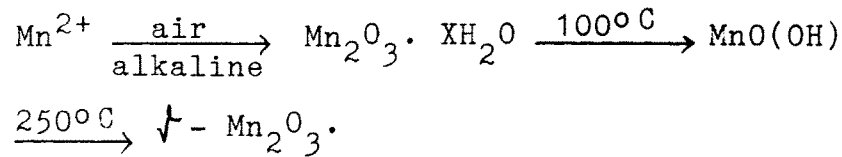
It is used as an ore of manganese, as an oxidizing agent in manufacture of chlorine, bromine and oxygen, as a drier in paints, a decolorizer in glass and in electric batteries, as coloring material in bricks, pottery, glass, etc.

$\underline{\text{Mn}_2\text{O}_3}$:

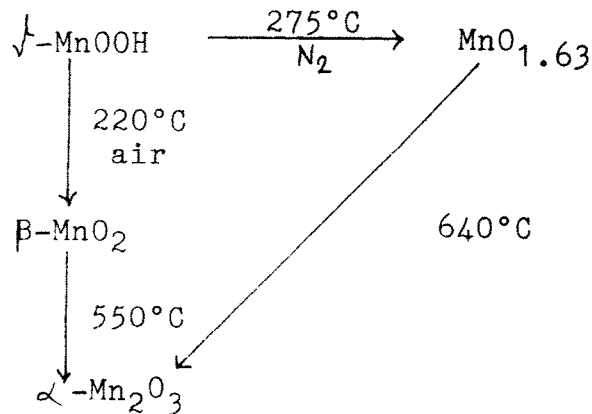


The reacting mixture is boiled and filtered, then after washing with water it is dried over P_2O_5 in vacuum at temperature below about 100°C . Careful dehydration of $\downarrow\text{-MnO}(\text{OH})$ in vacuum at 250° yields $\downarrow\text{-Mn}_2\text{O}_3$.

$\downarrow\text{-Mn}_2\text{O}_3$ is formed by treatment of a suspension of Mn_3O_4 in oxygen gas. $\downarrow\text{-Mn}_2\text{O}_3$ films can be prepared from MnCl_2 , NH_4Cl and NH_3 .



$\alpha\text{-Mn}_2\text{O}_3$ can be formed from MnSO_4 . The mixture of MnSO_4 , H_2O_2 and aqueous ammonia produces $\downarrow\text{-MnOOH}$ in air, which undergoes the following reactions on heating /10/



It has tetragonal structure (for braunite) and orthorhombic structure (for manganite).

It is antiferromagnetic, amphoteric, semiconducting oxide. It has resistivity greater than $10^9 \Omega \text{ cm}$. Little

else has been measured on this material.

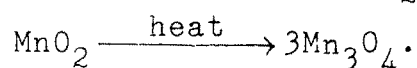
It is used as an ore of manganese.

$\underline{\text{Mn}_3\text{O}_4}$ ($\text{MnO}, \text{Mn}_2\text{O}_3$) :

MnF_3 , $\text{Mn}_2(\text{SO}_4)_3$ and Mn_2O_3 contain Mn^{+3} and they are hydrolyse in water.



It is formed by heating MnO_2 /11/



It has a tetragonal or tetragonally deformed spinel structure.

It is paramagnetic, amphoteric, semiconducting oxide. It is an insulator with room-temperature conductivity of the order of $10^{-7} \Omega^{-1} \text{cm}^{-1}$ /9/. This should have poor conductivity if electron exchange between ions whose valencies differ by two is unlikely. However, there seems to be no reason why a process of two electrons simultaneously hopping through the crystal should not produce a greater room temperature conductivity than $10^{-7} \Omega^{-1} \text{cm}^{-1}$.

It is used as an ore of manganese.

1.5 Statement of the Problem :

In recent years, importance of oxide (ZnO , MnO , CrO_2 , Fe_2O_3 , WO_3 , YBaCuO , SiO_2 , TiO_2 , SnO_2 , etc.) films has been increased as they are effectively used in ECPV cell, photo-electrolysis of water, photoluminescence, insulator, thermistor, resistor and recently as a superconductor. During the last decade the interest in transition metal

oxides in the form of thin films has been considerably increased. Out of different transition metal oxides, manganese oxide films are found to be interesting. Mn-oxide electrode has a promising character for practical use in water electrolysis/12/. Thus it is promising to study whether the Mn-oxide films are helpful in electrochemical photovoltaic effect and in superconducting phenomenon. In view of this Mn-oxide films will be prepared by chemical bath deposition/13/ and spray pyrolysis /14/. Very little attention has been paid to the study of structural, electrical and optical properties of Mn-oxide films, in detail. Also very few reports are available on electrical and optical properties of Mn-oxide films.

In the present investigation, the Mn-oxide films were planned to prepare by spray pyrolysis method, on amorphous glass and conducting glass substrates, as this method is a low cost process of preparing this films from a wide variety of materials. This process was developed in the early 1960's by Hill Chamberlin/15/ for preparing thin polycrystalline films. The preparative parameters, like substrate temperature, concentration, spray rate, will have to be optimized in order to get good quality films. The effect of all these parameters on structural, electrical, optical and electrochemical properties will be studied. Mn-oxide films will also be deposited on glass substrates by chemical bath deposition method.

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