CHAPTER 1

INTRODUCTION
1.1 Introduction

Inorganic glasses are compelling materials to study from a fundamental point of view as they pose challenging and yet unsolved problems in the field of condensed matter physics. Ranging from silicates to halides and chalcogenides, inorganic glasses have found amazingly widespread use in our lives that ranges from windshields, flat-panel displays and electric bulbs all the way to optical fibers and amplifiers in modern day telecommunication networks. Vitreous materials like silica, boric oxide and soda-lime-silica glass are the classic materials from which both the physics of the amorphous state and the modern concepts of atomic structure of glass originated [1-3]. From a historical standpoint silicate glasses are the most ancient materials known to mankind. They also occur naturally, predominantly amongst volcanic rocks and indeed offer important insight into the physico-chemical conditions in the interior of our planet. At the other extreme, chalcogenide and halide glasses represent some of the most recent functional materials to be discovered. The science of glass making continues to advance. New methods are being discovered to produce glass faster and better; more uses for it are being found in computers, medical devices and communications, to name a few.

1.1.1 Glass

A glass is defined as ‘an inorganic product of fusion which is cooled to a rigid condition without crystallizing’. In its broadest sense, glass is an amorphous solid that, unlike a crystal, lacks periodicity in its atomic structure (Fig. 1.1). Glass is a state of matter that combines the rigidity of crystals with the random molecular structure of liquids. They have the mechanical rigidity of crystals, but the random disordered arrangement of molecules that characterizes liquids. Hence the properties of glasses are as versatile as their composition. Glass can be made
with excellent homogeneity in a variety of forms and sizes, from small fibers to meter-sized pieces. Furthermore, glass can be doped with transition metal, rare earth ions and micro crystallites and a wide range of properties can be chosen to meet the needs of various applications. These advantages over crystalline materials are based on the unique structural and thermodynamic features of glass materials. Glass science, therefore, has significantly been progressive with the development of many new glassy materials as novel optical materials [4-9].

![Fig. 1.1 Arrangement of atoms in crystalline and amorphous materials](image)

**1.1.2 Glass forming ability**

Glasses are very special materials that are formed only under suitable thermodynamic conditions. When a liquid is cooled from high temperature, crystallization may take place at melting point $T_m$, where its volume changes abruptly. When a liquid is super cooled, the glass transformation takes place below the melting point $T_m$, where a gradual break in slope occurs. The region over which the change in slope occurs is known as glass transition temperature $T_g$. The glass transition temperature is the temperature above which the glass solid starts behaving like a viscoelastic solid. It is normally described on the basis of either
enthalpy or volume versus temperature diagrams as in Fig. 1.2. The most commonly measured signature of glass transition is the rapid increase in specific heat $C_p$ across a relatively narrow temperature range when a glass is reheated into the super cooled liquid state in a scanning calorimeter (Fig. 1.3). The characteristic temperature associated with this jump, $C_p$ is also known as the calorimetric glass transition temperature $T_g$. It is interesting to note in this regard that the variation with temperature of the thermodynamic properties such as enthalpy, volume or specific heat across the glass transition, depends on the cooling or heating rate of the liquid. The structure of a rapidly cooled glass is more open than that of a slowly cooled one because the ‘freezing-in’ of the atomic arrangement occurs at a higher temperature. The properties of a glass are therefore different from glass to glass, depending on the thermal history, even if the chemical composition is the same.

![Figure 1.2 Variation of specific volume as a function of temperature](image)

**Fig. 1.2** Variation of specific volume as a function of temperature
1.1.3 The structure of glasses

Zachariasen [3] coined the name network-forming cations which according to his rules in association with oxygen form the random network of glasses. The term network former is generally adopted for oxides capable of glass formation. Oxygen ions which act as bridges between the structural units are called Bridging oxygens (BO). Oxides $A_2O$ or $AO$, where $A$ is a metal atom, do not satisfy any rules of Zachariasen. Oxides $A_2O_3$ satisfy the rules if the oxygen atoms form triangles around each $A$ atom and $AO_2$ or $A_2O_5$ satisfy these rules if the oxygen atoms form tetrahedra around each $A$. From these considerations Zachariasen concluded that the following oxides should be glass formers: $B_2O_3$, $SiO_2$, $GeO_2$, $P_2O_5$, $As_2O_3$, $Sb_2O_3$, $V_2O_5$, $Sb_2O_5$, $P_2O_3$, $As_2O_5$, $Nb_2O_5$ and $Ta_2O_5$.

In addition to the network former, glasses may contain oxides which do not participate in forming the network structure and are called network modifiers.
There are three principal actions of network modifiers in glasses, which can be summarized for an $\text{A}_2\text{O}_3$ glass as follows (Fig. 1.4):

a. Breaking of A-O-A bonds and creation of non-bridging oxygens

b. Increasing the oxygen coordination of cation A

c. Combination of both

The modifiers (calcium, lead, lithium, sodium, potassium) alter the network structure; they are usually present as ions, compensated by nearby non-bridging oxygen atoms, bound by one covalent bond to the glass network and holding one negative charge to compensate for the positive ion nearby. The intermediates (titanium, aluminium, zirconium, beryllium, magnesium, zinc) can act as both network formers and modifiers, according to the glass composition.

Fig. 1.4 Structure of a glass with modifier oxide
1.1.4 Borate glasses

Boron is an important metalloid whose atomic mass and atomic number are 10.81 and 5, respectively. There are two stable boron isotopes, $^{10}$B and $^{11}$B, which are naturally present at 19.10 - 20.31 % and 79.69 - 80.90 %, respectively. Boron has electronic structure $1s^22s^22p^1$ and an expected valence of three. Boron also has a high affinity for oxygen-forming borates, polyborates, borosilicates, peroxoborates etc. In nature, boron is an abundant mineral with combination of oxygen and various alkaline and alkaline earth metals e.g., Na, Ca and Mg.

Among several glass systems, oxide glasses are the most stable active ion hosts for practical applications such as optical and sensor devices, mainly due to their high chemical durability and thermal stability. Borate glasses are the focus of interest due to their structure and properties and are very well known for their glass forming ability. Boric oxide ($B_2O_3$) acts as a best glass former, because of its higher bond strength, lower cation size and smaller heat of fusion. Borate glasses possess scientific interest because of the occurrence of boron anomaly and are incorporated into various glass systems as flux materials to attain materials of high technological application [10-15]. They also exhibit high solubility and are choice glasses for sequestering radioactive waste. This versatility derives from the flexibility of their atomic structure to accommodate other glass-formers, in addition to glass modifiers. The borate compounds represent appropriate host materials for investigating the nature and structure of the luminescence and paramagnetic centres; because practically all borates, including tetraborates can be obtained in both crystalline and glassy phases. Several works have been performed on borate glasses to study their structure, magnetic and electrical properties [16-20]. The glassy material which consists of heaviest metal oxides is more promising for photonics and optoelectronics.
1.1.5 Alkali zinc borate glasses

Borate glasses have a more complex action of alkali ions than silicate glasses. In mixed-alkali glass systems, the glass-transition temperature $T_g$ can exhibit positive or negative deviation from linearity. The glass-transition temperature of borate glasses is linked with the atomic arrangements present in the glass system. Shelby, Button et al., Martin et al., linked the decrease in $T_g$ with the growth of boron with non-bridging oxygens in the high-alkali region. Raman studies confirmed that, as the size of the alkali ion increases, formation of non-bridging oxygen is favored in the glass system [21-23]. Formation of non-bridging oxygen units causes depolymerization of the oxide network. In the alkali borate glass systems, each alkali oxide is associated with a proportional quantity of B$_2$O$_3$; so that, the number of the structural units depends on both the nature and the total concentration of the added modifiers and can often give rise to tightly organized structures resulting in intermediate order.

High electrical conductivity and ease in preparation of alkali-borate glasses has suggested them as potential fast ion conducting solid electrolytes. Of these, lithium-borate glasses have been studied most. The conductivity in this glass system increases as the mole fraction of lithium oxide is increased. While maintaining the vitreous nature, further increase in conductivity is achieved by adding lithium in the form of halides or other lithium salts.

ZnO is often called an II-VI semiconductor because zinc and oxygen belong to the II and VI groups of the periodic table, respectively. It is a well-known n-type, direct wide bandgap semiconductor with band gap of 3.37 eV and a large excitonic binding energy of 60 meV at room temperature [24-26]. The direct wide bandgap of ZnO makes the semiconductor a good candidate for optoelectronic applications and the large exciton energy helps to employ the excitonic recombination process as a lasing mechanism [27]. This semiconductor
has several favorable properties: good transparency, high electron mobility, wide band gap and strong room temperature luminescence etc.

1.1.6 Structure of borate/alkali borate glasses

The structure of the simplest borate glass \( (\text{B}_2\text{O}_3) \) consists of planar \( \text{B}_3\text{O}_6 \) boroxol rings made of three corner-shared \( \text{BO}_3 \) triangles (Fig. 1.5). These rings are connected to one another by a small non-ring population of \( \text{BO}_3 \) triangles. Approximately 75-80 % of B atoms belong to these boroxol rings, indicating the presence of substantial intermediate range order in \( \text{B}_2\text{O}_3 \) glass [28]. Initial addition of modifier ions such as alkalis and alkaline-earths to \( \text{B}_2\text{O}_3 \) glass results in the conversion of \( \text{BO}_3 \) units into \( \text{BO}_4 \) units without the formation of any non-bridging oxygen [29-33]. This contrasts sharply with silicate glasses where NBOs are generated in proportion to the concentration of modifiers. In borate glasses, the concentration of \( \text{BO}_4 \) units, \( N_4 \), that increases with alkali concentration, \( x \) reaching a maximum at \( x \sim 1/3 \) or \( R \sim 0.5 \), where \( R = x/(1-x) \) is the molar ratio of alkali oxide: \( \text{B}_2\text{O}_3 \). However, when \( R \) exceeds 0.5 this results in a decrease in the \( \text{BO}_4 \) concentration, with the formation of \( \text{BO}_3 \) units incorporating NBOs that results in a loss of connectivity and rigidity of the structure according to the reaction [29-33]:

\[
\text{BO}_4 \rightarrow \text{BO}_3 + \text{NBO}
\]

The peak in \( \text{BO}_4 \) configurations in alkali borates can be clearly seen in Fig. 1.6. The primary structural units are trigonal planar (\( \text{BO}_3 \)) and tetrahedral (\( \text{BO}_4 \)) and they may exist as isolated anions, connect each other by sharing oxygen to form rings and cages, or form finite clusters, infinite chains, sheets and frameworks. Boric acid (sassolite), borax (tincal), kernite, colemanite, ulexite, probertite, hydroboracite, datolite and szaibelyite (ascharite) are the boron minerals which have commercial importance. Borate compounds show an ionic character as they contain a boron oxoanion, such as the metaborate anion
[B(OH)₄]⁻ in combination with cationic species, such as Na⁺, Li⁺. Table 1.1 lists a number of well-known borate anions, including the structural formula and resolved oxide formula for the corresponding compounds formed in combination with monovalent cations (represented by $M^+$).

Chemical structures of these oxoanions are different from each other. For example, the metaborate anion has a tetrahedral form, while the tetraborate anion is a bridged eight member B-O ring, the triborate anion is a six member B-O ring referred as a boroxyl ring, the pentaborate anion consists of two six-member B-O ring sharing a common boron atom and the hexaborate anion consists of three B-O rings that share three boron atoms and one oxygen atom [34]. Schematic representations of these structures are given in Fig. 1.7. The B-O bond distance is 0.137 nm. The bonding distance between the layers is ~ 0.43 nm, which is a much greater distance; thus the bonds are weaker. The strong B-O bonds within the planar structure retain a two-dimensional configuration, while the weaker inter-sheet bonds permit relatively easy sliding.
Fig. 1.6 Fraction of B atoms present as BO$_4$ species ($N_4$) in alkali borate glasses

Table 1.1 Borate anions and their structures

<table>
<thead>
<tr>
<th>Boron oxoanion</th>
<th>Common name</th>
<th>Structural formula bearing metal cation, $M^+$</th>
<th>Resolved oxide formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>[B(OH)$_4$]$^{-}$</td>
<td>metaborate</td>
<td>$M$[B(OH)$_4$]</td>
<td>$M_2O$·B$_2$O$_3$·4H$_2$O</td>
</tr>
<tr>
<td>[B$_4$O$_5$(OH)$_4$]$^{-}$</td>
<td>tetraborate</td>
<td>$M_2$[B$_4$O$_5$(OH)$_4$]</td>
<td>$M_2O$·2B$_2$O$_3$·4H$_2$O</td>
</tr>
<tr>
<td>[B$_5$O$_6$(OH)$_4$]$^{-}$</td>
<td>pentaborate</td>
<td>$M_2$[B$_5$O$_6$(OH)$_4$]</td>
<td>$M_2O$·5B$_2$O$_3$·4H$_2$O</td>
</tr>
<tr>
<td>[B$_3$O$_3$(OH)$_4$]$^{-}$</td>
<td>triborate</td>
<td>$M_2$[B$_3$O$_3$(OH)$_4$]</td>
<td>$M_2O$·3B$_2$O$_3$·4H$_2$O</td>
</tr>
<tr>
<td>[B$_3$O$_3$(OH)$_5$]$^{-}$</td>
<td>triborate</td>
<td>$M_2$[B$_3$O$_3$(OH)$_5$]</td>
<td>2$M_2O$·3B$_2$O$_3$·5H$_2$O</td>
</tr>
<tr>
<td>[B$_6$O$_7$(OH)$_6$]$^{-}$</td>
<td>hexaborate</td>
<td>$M_2$[B$_6$O$_7$(OH)$_6$]</td>
<td>$M_2O$·3B$_2$O$_3$·3H$_2$O</td>
</tr>
</tbody>
</table>
Lithium is used in high-capacity energy storage devices for next-generation electric vehicles, in light weight high-power-density lithium ion batteries for heart pacemakers, mobile phones and laptop computers [35, 36] and as blanket breeding material for deuterium-tritium fusion reactors [37]. Diffusion and ionic conduction in Li\textsubscript{2}O are subjects of great interest due to the superionic behavior of this material. Lithium ions, in turn, are coupled with the anion subsystem by an ionic bond that may result in the appearance of ionic conductivity and of superionic properties.
Fig. 1.8 (a) shows the unrelaxed structure of defective Li$_2$O where the migrating Li$^+$ and the vacancy (V) are in their original positions. Fig. 1.8 (b) shows the symmetric transition structure. The lithium ion is centred between two oxygen ions. The final structure (Fig. 1.8 (c)), where the migrating ion has accessed the position of the vacancy, is isoenergetic with the starting structure. Li$^+$ is in the vacancy position while the vacancy is in the original position of the Li$^+$. 

**Fig. 1.8** Li$^+$ migration process in Li$_2$O. In (a) the Li$^+$ and vacancy (V) are in their original positions, in (b) the transition state and in (c) the migrating
1.2 Mixed Alkali Effect: Scope of the present work

One of the most widely studied component interactions in glasses is the mixed-alkali effect (MAE). In oxide glasses, where two dissimilar alkali species coexist, many physical properties, most notably ionic conductivity and viscosity, demonstrate remarkable deviation from the linearity when one alkali cation substitutes another at total fixed concentration of alkalis. This phenomenon is usually referred to as mixed alkali effect, mixed cation effect and although it is known since a long time there is no general agreement concerning its origin. Cations in glass are primarily responsible for the determining their local environment. Each cation tends to be surrounded regularly and densely by anions at distances depending on the respective cation size. For example, Li$^+$ shows a strong tendency to fourfold co-ordination with oxygen atoms, whereas for Na$^+$ the most frequent coordination with oxygen is five or six, for K$^+$ the preferred coordination number is six to eight and for Cs$^+$ it is eight to twelve.

MAE is observed when two or three types of alkali ions are introduced into a glassy network. MAE is found in various glass systems like bismuthate, arsenate, tungstate and borate glasses. The strength of the MAE depends on many factors, e.g., temperature, total alkali content, size and mass difference of the involved alkali ions, etc. It has also been reported that the magnitude of the MAE increases with the difference in size or mass of the involved alkali ions. Most technical glasses containing a variety of different cations, but almost all studies on MAE are focused on glasses with only two kinds of ions. Mixed alkali glasses also show a unique mechanical relaxation phenomenon at temperatures of 100-200 °C. The non-linear and non-statistical variation in the concentration of BO$_3$ and BO$_4$ units with alkali oxide concentration results in a corresponding compositional variation of physical properties in binary alkali borate glasses.
Glass system of composition Li₂O-Na₂O-B₂O₃:Fe₂O₃ with replacing alkali oxides one by another has been prepared and the dielectric properties (constant ε', loss tan δ, a.c. conductivity σac over a wide range of frequency and temperature) of these glasses have also been explored to identify MAE [38]. Recently the mixed alkali effects on the devitrify cation behavior and thermal stability of the xNa₂O:(50−x)Li₂O:50P₂O₅ glass system, where Li⁺ are progressively substituted with Na⁺ in the glass matrix, keeping the whole alkali ion concentration constant. In this regard, the dependence of glass transition temperature, Tg and crystallization temperature, Tc, on the heating rate with varying composition has been studied and the activation energy of thermal relaxation has been deduced. Spectroscopic investigations on divalent transition metal ions (Cu²⁺, VO²⁺, Ni²⁺, Co²⁺, Mn²⁺) doped 19.9 ZnO + x Li₂O + (30−x) Na₂O + 50B₂O₃ (5≤ x ≤ 25) (ZLNB) glasses were studied and mixed alkali effect is explained evidently [39- 44]. When mixed with glass modifiers, such as Li₂CO₃ or other alkali oxides, the internal structure of B₂O₃ is rearranged due to the formation of non-bridging oxygens. According to previous studies, ZnO-B₂O₃ glasses exhibit low melting point, so they are of special interest owing to their applications in different fields of electronic products. This is due to the fact that higher the polarizability of an ion, lower the melting temperature of the substance. Kajinami et al., [45] investigated the structure of (ZnO)x(B₂O₃)1−x by X-ray diffraction (XRD). The authors found that zinc ions are surrounded by four oxygen atoms and formed a tetrahedral structure whose Zn-O distance is about 2Å and the neighboring structure of boron atoms transforms from BO₄ tetrahedral to BO₃ trigonal structures with increasing of the zinc oxide content.

In order to establish a specific indication of all the features of mixed alkali effect, the physical and spectral investigations on Li-Na zinc borate glasses (ZLNB) have been carried out in the present work. All the mixed alkali zinc borate glasses are prepared by melt quenching and their properties have been studied by
spectroscopic techniques. The addition of alkali oxides modifies the boroxol rings, complex borate groups with one or two borate atoms, with four-coordination are formed [46]. The alkali oxides may improve the physical properties of these glasses. ZnO enters the glass structure in the form of both network former and network modifier. Another interesting aspect of local order in borate glasses includes the unusual coordination environments of transition metal oxides. In particular, intermediate cations can now be seen as occupying sites at the interface between the network and the modifiers in the glass structure, influencing the solubility of other ions in the melt by changing their coordination, the chemical strength of the glass and also the color. The changes in alkali borates follow the gradual appearance of BO$_4$ units surrounded by bridging oxygens to which the transition metals coordinate to form rigid domains. As the tetraborate anions are replaced by BO$_3$ units with NBOs and associated alkalis, transition metal ordering diversifies with the introduction of the structurally more flexible four- and five-fold polyhedra. The addition of any transition metal oxide makes these glasses semi-conducting in nature.
1.3 Spectroscopy of transition metal ions

Transition metals differ from main group metals in several key properties. One of the more interesting aspects of transition metals is their ability to form coordination compounds. Coordination compounds are formed between a metal atom or ion and a molecule with one or more unshared electron pairs, called a ligand. Anions as well as neutral molecules may act as ligands. If one or more neutral molecules coordinate to metal ion, the resulting species retains the charge of the transition metal ion and is called a complex ion. There are a number of properties shared by the transition elements that are not found in other elements, which results from the partially filled d shell. These include

- The formation of compounds whose color is due to d-d electronic transitions
- The formation of compounds in many oxidation states, due to the relatively low reactivity of unpaired d electrons.
- The formation of many paramagnetic compounds due to the presence of unpaired d electrons.

A characteristic of transition metals is that they exhibit two or more oxidation states, usually differing by one. The oxidation states of the transition metal ions are listed in Table 1.2. Free ion terms for $d^{1-10}$ configurations are given in Table 1.3. Transition metal ions with configurations $d^2 - d^8$ have more than one free-ion term. From the group theory, the splitting of various electronic states of free atom or ion subjected to octahedral ligand environment can be predicated and they are shown in Table 1.4. The transition elements and their ionic radii are listed in Table 1.5.
Table 1.2 Oxidation states of transition metal ions

<table>
<thead>
<tr>
<th>Transition metal ion</th>
<th>Atomic number</th>
<th>Outer electronic configuration</th>
<th>Oxidation states</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
<td>21</td>
<td>$3d^1 4s^2$</td>
<td>+2, +3</td>
</tr>
<tr>
<td>Ti</td>
<td>22</td>
<td>$3d^2 4s^2$</td>
<td>+2, +3, +4</td>
</tr>
<tr>
<td>V</td>
<td>23</td>
<td>$3d^3 4s^2$</td>
<td>+2, +3, +4, +5</td>
</tr>
<tr>
<td>Cr</td>
<td>24</td>
<td>$3d^4 4s^2$</td>
<td>+1, +2, +3, +4, +5, +6</td>
</tr>
<tr>
<td>Mn</td>
<td>25</td>
<td>$3d^5 4s^2$</td>
<td>+2, +3, +4, +5, +6</td>
</tr>
<tr>
<td>Fe</td>
<td>26</td>
<td>$3d^6 4s^2$</td>
<td>+2, +3, +4, +5, +6</td>
</tr>
<tr>
<td>Co</td>
<td>27</td>
<td>$3d^7 4s^2$</td>
<td>+2, +3, +4</td>
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<td>Ni</td>
<td>28</td>
<td>$3d^8 4s^2$</td>
<td>+2, +3, +4</td>
</tr>
<tr>
<td>Cu</td>
<td>29</td>
<td>$3d^{10} 4s^1$</td>
<td>+1, +2</td>
</tr>
<tr>
<td>Zn</td>
<td>30</td>
<td>$3d^{10} 4s^2$</td>
<td>+2</td>
</tr>
<tr>
<td>Mo</td>
<td>42</td>
<td>$4d^5 5s^1$</td>
<td>+2, +3, +4, +5, +6</td>
</tr>
</tbody>
</table>

Table 1.3 Free ion terms for $d^{1-10}$ configurations

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Terms</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d^1$, $d^9$</td>
<td>$^2D$</td>
</tr>
<tr>
<td>$d^2$, $d^8$</td>
<td>$^3F$, $^3P$, $^1G$, $^1D$, $^1S$</td>
</tr>
<tr>
<td>$d^3$, $d^7$</td>
<td>$^4F$, $^4P$, $^2H$, $^2G$, $^2F$, $^2D(2)$, $^2P$</td>
</tr>
<tr>
<td>$d^4$, $d^6$</td>
<td>$^5D$, $^3H$, $^3G$, $^3F(2)$, $^3D$, $^3P(2)$, $^1I$, $^1G(2)$, $^1F$, $^1D(2)$, $^1S(2)$</td>
</tr>
<tr>
<td>$d^5$</td>
<td>$^6S$, $^6G$, $^4F$, $^4D$, $^4P$, $^2I$, $^2H$, $^2G(2)$, $^2F(2)$, $^2D(3)$, $^2P$, $^2S$</td>
</tr>
</tbody>
</table>
Table 1.4 Transformation of S, P, D, F, G, H and I terms in octahedral field

<table>
<thead>
<tr>
<th>Free ion term</th>
<th>Number of states</th>
<th>Terms in $O_h$</th>
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<tbody>
<tr>
<td>S</td>
<td>1</td>
<td>$A_{1g}$</td>
</tr>
<tr>
<td>P</td>
<td>3</td>
<td>$T_{1g}$</td>
</tr>
<tr>
<td>D</td>
<td>5</td>
<td>$E_g + T_{2g}$</td>
</tr>
<tr>
<td>F</td>
<td>7</td>
<td>$A_{2g} + T_{1g} + T_{2g}$</td>
</tr>
<tr>
<td>G</td>
<td>9</td>
<td>$A_{1g} + E_g + T_{1g} + T_{2g}$</td>
</tr>
<tr>
<td>H</td>
<td>11</td>
<td>$E_g + 2T_{1g} + T_{2g}$</td>
</tr>
<tr>
<td>I</td>
<td>13</td>
<td>$A_{1g} + A_{2g} + E_g + T_{1g} + 2T_{2g}$</td>
</tr>
</tbody>
</table>

Table 1.5 Transition elements and their ionic radii

<table>
<thead>
<tr>
<th>Element</th>
<th>State</th>
<th>Ionic radii (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
<td>Sc$^{3+}$</td>
<td>0.70</td>
</tr>
<tr>
<td>Ti</td>
<td>Ti$^{3+}$</td>
<td>0.76</td>
</tr>
<tr>
<td>V</td>
<td>V$^{4+}$</td>
<td>0.63</td>
</tr>
<tr>
<td>Cr</td>
<td>Cr$^{3+}$</td>
<td>0.63</td>
</tr>
<tr>
<td>Mn</td>
<td>Mn$^{2+}$</td>
<td>0.80</td>
</tr>
<tr>
<td>Fe</td>
<td>Fe$^{2+}$</td>
<td>0.76</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td></td>
<td>0.64</td>
</tr>
<tr>
<td>Co</td>
<td>Co$^{2+}$</td>
<td>0.72</td>
</tr>
<tr>
<td>Ni</td>
<td>Ni$^{2+}$</td>
<td>0.69</td>
</tr>
<tr>
<td>Cu</td>
<td>Cu$^{2+}$</td>
<td>0.72</td>
</tr>
<tr>
<td>Zn</td>
<td>Zn$^{2+}$</td>
<td>0.74</td>
</tr>
<tr>
<td>Mo</td>
<td>Mo$^{5+}$</td>
<td>0.61</td>
</tr>
</tbody>
</table>
1.3.1 Optical absorption spectroscopy

Optical radiation interacts with materials in a variety of ways depending upon the material and the wavelength of the optical radiation, giving rise to the optical spectra, which could be either emission or absorption spectra in solids, normally it is the absorption spectrum that is observed. This is nothing but the variation of the radiation intensity as a function of wavelength. Study of the absorption spectra of transition metal ions embedded in solids had been extensively used to obtain information about the local symmetry in which the ion sits its valence state, its site preference and determination of the degree of covalency of the metal-ligand bond. The d electrons are affected by the bonding electrons and are affected by the d electrons. The effects of the bonding electrons upon the d electrons are addressed within the subjects of crystal field theory or ligand field theory. They are concerned with the d-electron properties that observe in spectral and magnetic measurements.

Crystal field theory (CFT) is a model that describes the breaking of degeneracies of electronic orbital states, usually d or f orbitals, due to a static electric field produced by a surrounding charge distribution (anion neighbors). This theory has been used to describe various spectroscopies of transition metal coordination complexes, in particular optical spectra (colors). CFT was developed by physicists Hans Bethe and John Hasbrouck van Vleck [47] in the 1930’s. CFT was subsequently combined with molecular orbital theory to form the more realistic and complex ligand field theory (LFT), which delivers insight into the process of chemical bonding in transition metal complexes.

According to CFT, the interaction between a transition metal and ligands arises from the attraction between the positively charged metal cation and negative charge on the non-bonding electrons of the ligand. As a ligand approaches the metal ion, the electrons from the ligand will be closer to some of
the d-orbitals and farther away from others causing a loss of degeneracy. The electrons in the d-orbitals and those in the ligand repel each other due to repulsion between like charges. Thus the d-electrons closer to the ligands will have a higher energy than those further away which results in the d-orbitals splitting in energy. This splitting is affected by the following factors:

- The nature of the metal ion
- The metal’s oxidation state: a higher oxidation state leads to a larger splitting
- The arrangement of the ligands around the metal ion
- The nature of the ligands surrounding the metal ion. The stronger the effect of the ligands then the greater the difference between the high and low energy d groups

The most common type of complex is octahedral; here six ligands form an octahedron around the metal ion. In octahedral symmetry the d-orbitals split into two sets with an energy difference, $\Delta_{\text{oct}}$ (10 Dq) where the $d_{xy}$, $d_{xz}$ and $d_{yz}$ orbitals will be lower in energy than the $d_{z^2}$ and $d_{x^2-y^2}$, which will have higher energy, because the former group is farther from the ligands than the latter and therefore experience less repulsion. The three lower-energy orbitals are collectively referred to as $t_{2g}$ and the two higher-energy orbitals as $e_g$ (Fig. 1.9). Also the spatial orientation of d orbitals shows that the $d_{z^2}$ and $d_{x^2-y^2}$ orbitals point directly at the corners of an octahedron (Fig. 1.10). The triply degenerate set has the symmetry designation $t_{2g}$ and the doubly degenerate set has the designation $e_g$. These designations are from the character table for the octahedral symmetry group $O_h$. 
Fig. 1.9 Octahedral crystal field splitting

Fig. 1.10 Spatial orientation of d-orbitals in octahedral complex
Fig. 1.11 Tetrahedral crystal field splitting

Fig. 1.12 Spatial orientation of d-orbitals in tetrahedral complex
Tetrahedral complexes are the second most common type; here four ligands form a tetrahedron around the metal ion. In a tetrahedral crystal field splitting the d-orbitals again split into two groups, with an energy difference of $\Delta_{\text{tet}}$ where the lower energy orbitals will be $d_{z^2}$ and $d_{x^2-y^2}$ and the higher energy orbitals will be $d_{xy}$, $d_{xz}$ and $d_{yz}$ (Fig. 1.11 & 1.12) that are opposite to the octahedral case. Furthermore, since the ligand electrons in tetrahedral symmetry are not oriented directly towards the d-orbitals, the energy splitting will be lower than in the octahedral case. Square planar and other complex geometries can also be described by CFT. Distortions in octahedral complexes can undergo tetragonal distortions (the elongation of the z-axis and shortening of the x and y axes) to become elongated into molecules with square planar ($D_{4h}$) symmetry. As the z-axis is elongated, the degeneracy between the $d_{z^2}$ and $d_{x^2-y^2}$ orbitals is broken, with the $d_{z^2}$ orbital lower in energy since the ligands are further away.

The splitting of d-orbitals in the crystal field model not only depends on the geometry of the complex, it also depends on the nature of the metal ion, the charge on this ion and the ligands that surround the metal. Some ligands always produce a small value of $\Delta$, while others always give a large splitting. The reasons behind this can be explained by ligand field theory. The spectro-chemical series is an empirically derived list of ligands ordered by the size of the splitting $\Delta$ that they produce:

$$\Gamma^- < Br^- < S^{2-} < SCN^- < Cl^- < NO_3^- < N_3^- < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < CH_3CN < py < NH_3 < en < phen < NO_2^- < PPh_3 < CN^- < CO$$

Ligands that give rise to large differences between the energies of the $t_{2g}$ and $e_g$ orbitals are called strong-field ligands. Those at the opposite extreme are known as weak field ligands. The use of these splitting diagrams can aid in the prediction of the magnetic properties of coordination compounds. A compound that has unpaired electrons in its splitting diagram will be paramagnetic and will be attracted by magnetic fields, while a compound that lacks unpaired electrons in
its splitting diagram will be diamagnetic and will be weakly repelled by a magnetic field. The force of attraction between paramagnetic complexes and a magnetic field is proportional to the number of unpaired electrons in the complex. It can therefore determine whether a complex is high-spin or low-spin by measuring the strength of the interaction between the complex and a magnetic field.

### 1.3.2 Orgel diagrams

Orgel diagrams are correlation diagrams which show the relative energies of electronic terms in transition metal complexes, much like Tanabe-Sugano diagrams. Orgel diagrams are restricted to only weak field (i.e. high spin) cases, and offer no information about strong field (low spin) cases. Because Orgel diagrams are qualitative, no energy calculations can be performed from these diagrams. Also, Orgel diagrams show only the symmetry states of the highest spin multiplicity instead of all possible terms [48]. They give the number of spin allowed transitions, along with their respective symmetry designations. In an Orgel diagram, the parent term (P, D or F) in the presence of no ligand field is located in the center of the diagram, with the terms due to that electronic configuration in a ligand field at each side. There are two Orgel diagrams (Fig. 1.13 (a) & (b)), one for $d^1$, $d^4$, $d^6$ and $d^9$ configurations and the other with $d^2$, $d^3$, $d^7$ and $d^8$ configurations. The diagrams are applicable to tetrahedral as well as octahedral fields, using the principle that the d-orbital splitting pattern of one is the reverse of the other. These provide a summary of the splitting of the ground free-ion terms in the various cubic fields as well as excited terms with the same spin multiplicity.
Fig. 1.13 (a) Orgel diagram for energies of octahedral or tetrahedral terms arising from free ion D terms

Fig. 1.13 (b) Orgel diagram for energies of octahedral or tetrahedral terms arising from free ion F or P terms
1.3.3 Tanabe - Sugano diagrams

A term description for an atom/ion is more informative than its electron configuration because terms account for e-e repulsion energies. T-S diagrams are quantitative version of Orgel diagrams. T-S diagrams are used in coordination chemistry to predict absorptions in the UV, visible and IR electromagnetic spectrum of coordination compounds. T-S diagrams in general

(a) They contain all terms arising from a configuration, not just terms of highest spin-multiplicity.

(b) Appear different than Orgel diagrams because they use the ground symmetry state as a straight-line horizontal base, whereas Orgel diagrams place the parent term in a central location and direct ground symmetry states below it.

(c) Appear split for d⁴, d⁵, d⁶, d⁷ cases because both low and high spin symmetry states are included.

The x-axis of a T-S diagram is expressed in terms of the ligand field splitting parameter, Dq or Δ, divided by the Racah parameter B. The y-axis is in terms of energy E, also scaled by B. Three Racah parameters A, B and C describe various aspects of interelectronic repulsion. A is an average total interelectron repulsion; B and C correspond with individual d-electron repulsions. A is constant among d-electron configuration and it is not necessary for calculating relative energies, hence its absence from Tanabe and Sugano’s studies of complex ions. C is necessary only in certain cases and B is the most important of Racah’s parameters in this case. The diagrams can only be drawn if the ratio C/B is specified [49]. In these diagrams the zero of energy is always taken as that of the lowest term. Hence when there is a change of ground term, the diagram is discontinuous. The discontinuity always takes the form of an increase in the slope of term energies above a critical value of Dq/B. Some of the T-S diagrams for various d configurations are shown in the Fig. 1.14, 1.15 and 1.16.
Fig. 1.14 Energy level diagram for \(d^5\) configuration for \(C/B = 4.48\)
Fig. 1.15 Energy level diagram for d⁷ configuration for C/B = 4.63
1.3.4 Optical bandgap and Urbach energy

The optical band gap is the energy separating the valence band and the conduction band in a material and is recognized in the absorption spectrum as an abrupt increase in absorption. The bandgap of a semiconductor is always one of two types, a direct bandgap or an indirect bandgap (Fig. 1.17). The minimal-energy state in the conduction band and the maximal-energy state in the valence band are each characterized by a certain crystal momentum (k-vector) in the Brillouin zone. If the k-vectors are the same, it is called a direct gap. If they are different, it is called an indirect gap. The bandgap is called direct if the momentum of electrons and holes is the same in both the conduction band and the valence
band; an electron can directly emit a photon. In an indirect gap, a photon cannot be emitted because the electron must pass through an intermediate state and transfer momentum to the crystal lattice. A Tauc plot is used to determine the optical bandgap of the material from the absorption coefficient. Thus transmittance spectra must be converted to absorption coefficient $\alpha$, via

$$T = \exp(-\alpha d)$$

where $d$ is the thickness of the sample.

The Urbach rule [50-53], is obeyed in the region of the absorption spectrum of amorphous semiconductors. The existence of this region is explained by the exponential distribution of the density of localized states in the tails of allowed bands. The exponential tail at fundamental absorption edge is widely observed in many insulators. The tail of the spectra called the Urbach tail is empirically given as a function of photon energy $E$,

$$F(E) = A \exp\left\{-\sigma (E_o - E/K_B T)\right\}$$

Here $E_o$ and $\sigma$ are the convergence energy and the steepness parameter which are almost material constants at sufficiently high temperatures. The fundamental basis for the Urbach edge phenomena is its generality across the broad range of materials from amorphous silicon hydride to thallium chloride.
1.3.5 Electron Paramagnetic Resonance spectroscopy

Transition metal ions of 3d group exhibit different patterns of EPR signals depending on their electron spin and the crystalline environment. In the study of solid state materials, EPR method is employed to understand the symmetry of surroundings of the paramagnetic ion and the nature of its bonding to the nearest neighboring ligands. When a paramagnetic substance is placed in a steady magnetic field (H), the unpaired electron in the outer shell tends to align with the field. So the two fold spin degeneracy is removed. Thus the two energy levels, $E_{1/2}$ and $E_{-1/2}$ are separated by $g\beta H$, where $g$ is spectroscopic splitting factor and is called gyro magnetic ratio and $\beta$ is the Bohr magneton (Fig. 1.18). Since there is a finite probability for a transition between these two energy levels, a change in the
energy state can be stimulated by an external radio frequency. When microwave frequency ($\nu$) is applied perpendicular to the direction of the field, resonance absorption will occur between the two split spin levels. The resonance condition is given by,

$$\hbar \nu = g \beta H$$

Where $\hbar$ is Planck’s constant and $\beta = \frac{e\hbar}{2mc}$. The resonance condition can be satisfied by varying $\nu$ or $H$. However, EPR studies are carried out at a constant frequency ($\nu$), by varying magnetic field ($H$). For a free electron, the $g$ value is 2.0023. Since $\hbar$ and $\beta$ are constants, one can calculate the $g$-factor. This factor determines the divergence of the Zeeman levels of the unpaired electron in a magnetic field and is characteristic of the spin system.

In the crystal systems, the electron spins couple with the orbital motions and the $g$ value is a measure of the spin and orbital contributions to the total magnetic moment of the unpaired electron and any deviation of magnetic moment from the free spin value is due to the spin orbit interaction. Kramer’s theorem deals with restrictions to the amount of spin degeneracy which can be removed by a purely electrostatic field. If the system contains an odd number of electrons, such an electrostatic field cannot reduce the degeneracy of any level below two. Each pair forms what is known as a Kramer’s doublet, which can be separated only by a magnetic field. For example, $Fe^{3+}$ and $Mn^{2+}$ belonging to $d^5$ configuration, exhibit three Kramer’s doublets labeled as $|\pm 5/2>$, $|\pm 3/2>$ and $|\pm 1/2>$. 

For perfectly octahedral site symmetry, the $g$-values do not change with orientation of the crystal. But $g$-values vary with the orientation in a low symmetry fields. In general, there exists three $g$-values corresponding to $x$, $y$, $z$ axes of the crystal: $g_x$, $g_y$ and $g_z$. In the case of a tetragonal site, $g_x = g_y$ and this $g$-value is often referred to as $g_A$. This value can be obtained when the external magnetic field is applied perpendicular to the principal axis ($z$-axis). When the magnetic
field is parallel to z-axis, the g-value $g_z$ is referred to as $g_\|$. Based on the g-values, the site symmetry of the central metal ion can be known.

If the central metal ion also possesses a non-zero nuclear spin I, then hyperfine splitting occurs as a result of the interaction between the nuclear magnetic moment and the electronic magnetic moment. The measurement of g-value and hyperfine splitting factor provides information about the electronic states of the unpaired electrons and also about the nature of the bonding between the paramagnetic ion and its surrounded ligands. If the ligands also contain non-zero nuclear spin, then the electron spin interacts with the magnetic moment of the ligands. Then one could expect super hyperfine EPR spectrum [54]. However, it is not possible to distinguish between orthorhombic and other lower symmetries. In the present investigation, transition metal ion doped samples have been used for EPR recordings and analyzed in the next chapters.

![Diagram of EPR absorption for a single spin](image)

**Fig. 1.18 EPR absorption for a single spin**
1.4 References


