Chapter -I

Introduction
1.1 Introduction

During the last three decades, optical spectroscopy has grown by leaps and bounds into a powerful tool of research in the field of science and technology. Spectroscopy is useful in the identification of structure and environment of atoms and molecules by analyzing the radiation emitted or absorbed by them. The broad definition of spectroscopy is the study of interaction of electromagnetic radiation with matter. Generally optical spectroscopy deals with the measurement and interpretation of optical spectra arising from either emission or absorption of radiant energy by various substances. In emission spectroscopy, a molecule or atom experiences a transition from a higher energy state to lower energy state and emits energy as a photon. In absorption spectroscopy, transition takes place from lower energy level to higher energy level from the radiation field.

In recent years, spectroscopic investigations of crystals, glasses and solutions doped with transition metal and rare-earth ions play an important role in science and technology. RE$^{3+}$ ion doped glasses are used in the development of optical devices such as solid state lasers [1-4], phosphors and sensors [5-8], light converters [9-13], optical fiber amplifiers [14-17], optical storage devices [18-19] and spectral hole burning high density memories [20]. The prime interest in glasses is due to their relatively easy preparation compared to that of single crystals. In glasses wide range of concentrations can be studied and bulk samples can also be obtained for device fabrication [21-24]

1.2 Classification of solids

On the basis of atomic arrangement, solids may be broadly classified into two categories (1) crystalline and (2) amorphous.

In crystalline solids, both long-range and short-range order exists in the arrangement of atoms while in amorphous solids only short-range order exists. Fig. 1.1 shows the schematic representation of the ordered crystalline form and random network amorphous form of the same composition. Due to short-range periodicity
in the atomic arrangement, the degree of disorder will be greater in an amorphous solid than its crystalline counterpart and it will be having higher entropy compared to the crystalline phase. Therefore, amorphous state is a non-equilibrium state. So, on cooling from liquid phase to the solid phase, a crystalline solid is obtained as a transformation from one equilibrium state to another while in amorphous solid, the transformation is from an equilibrium state to a non-equilibrium state. Due to the random arrangement of atoms, amorphous materials exhibit isotropic properties while crystalline solids exhibit anisotropic properties.

Fig. 1.1: Atomic arrangements in (a) Crystalline and (b) Amorphous structures.

1.3 Definition of glass

Morey [25] defined glass as "an inorganic substance in a condition that is continuous with the liquid state, but which, as the result of a reversible change in viscosity during cooling, has attained so high a degree of viscosity as to be, for all practical purposes, rigid". The American Society for Testing for and Materials (ASTM) [26] define glass is "an inorganic product of fusion that has been cooled to a rigid condition without crystallization." However, these definitions do not explicitly address the character of a noncrystalline structure and the glass transformation behavior, two characteristics that separate glasses from other solids. In addition, glasses may be made by processes that do not necessarily produce liquids and so Shelby's definition seems most appropriate: Glass is a solid that possesses no long-range atomic order and, upon heating, gradually softens to the molten state [27].
1.4 Glass preparation and properties

Among the crystalline and amorphous phase of a material, the amorphous phase is less thermodynamically stable than the corresponding crystalline form. This means that amorphous phase posses a greater free energy. Hence the preparation of amorphous materials can be considered as the addition of excess of free energy to the crystalline polymorph. There are numerous techniques to prepare amorphous materials. Below given are the twelve widely used techniques for preparing materials in amorphous state.

1. Thermal Evaporation  
2. Sputtering  
3. Glow Discharge Decomposition  
4. Chemical Vapour Deposition  
5. Melt Quenching  
6. Gel desiccation  
7. Electrolytic Deposition  
8. Chemical Reaction  
9. Reaction Amorphization  
10. Irradiation  
11. Shock-wave transformation  
12. Shear Amorphization.

Among these techniques, the 'Melt-quenching' and 'Gel-desiccation' were frequently used for preparing glasses. Since the present thesis deals with glasses prepared by melt-quenching method, more emphasize is give to this technique. The other techniques including Gel-desiccation were explained by Elliott [28].

1.4.1 Melt quenching technique

The oldest method of producing amorphous solid is to cool the molten form of the material in sufficiently faster rates. The distinguishing feature of this process is that the amorphous solid is formed by the continuous hardening of the melt. On the other hand, crystallization of the melt occurs as discontinuous solidification. Hence the formation of glass is strongly dependent on the cooling rate of the melt. In order to get the glasses from the melt, the cooling rate should be high enough to bypass the crystal nucleation and growth. As the crystallization phase is more thermodynamically stable than the amorphous phase, crystal growth will dominate over the formation of amorphous phase, if allowed to take place freely. Turnbull [29] discussed in detail, the crystal nucleation and growth kinetics.
As said above, the cooling rate plays a dominant role in the glass formation. Further, the cooling rate required for glass formation depends on the constituents of the melt. For certain easy glass-formers, such as B$_2$O$_3$, very slow cooling rates (~ 1 KS$^{-1}$) are sufficient to form glass while certain other materials (such as metallic glasses) require very high cooling rates (~ 10$^5$ K S$^{-1}$).

In preparing the glasses with easy glass formers, a batch of finely powdered chemicals (~ 5 g) taken in a porcelain crucible will be placed in a furnace maintained at high temperatures. The melt will be stirred uniformly to get homogeneous liquid. After some time, the crucible will be taken out and the melt will be poured on a plate having good thermal conductivity (e.g., brass or copper); another plate will be placed over the melt, so that heat will be removed quickly from the melt. A cooling rate of the order of 10 KS$^{-1}$ will be achieved by this method and is sufficient for preparing most of the glasses.

Table 1.1

Different quenching techniques and their cooling rates

<table>
<thead>
<tr>
<th>Technique</th>
<th>Cooling rate (KS$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annealing</td>
<td>10$^5$ - 10$^2$</td>
</tr>
<tr>
<td>Air quenching</td>
<td>1 - 10</td>
</tr>
<tr>
<td>Liquid quenching</td>
<td>10$^2$ - 10$^3$</td>
</tr>
<tr>
<td>Splat cooling</td>
<td>10$^3$</td>
</tr>
<tr>
<td>Melt-spinning extraction</td>
<td>10$^6$ - 10$^8$</td>
</tr>
<tr>
<td>Evaporation</td>
<td>&lt; 10$^7$</td>
</tr>
<tr>
<td>Laser glazing</td>
<td>10$^{10}$ - 10$^{12}$</td>
</tr>
</tbody>
</table>

For certain other materials, especially metallic glasses, cooling rates produced in the above method are insufficient for producing glasses. Still higher cooling rates are required for such cases and these can be achieved by the use of a 'chill-block'. Klemant et al [30] were the first to use the "splat cooling technique", where quenching rate of the order of 10$^5$ KS$^{-1}$ can be achieved. This technique employs a method of projecting small droplets of liquid on a Cu-sheet. Table 1.1 lists the
various quenching techniques used to prepare glasses and their cooling rates. The conventional annealing technique is also included in the table to have a comparison between this and the different quenching techniques.

1.4.2 Properties of the glasses

The physical properties of a given specimen of glass may depend upon the previous history of the specimen. This is particularly the case for the mechanical strength under tension; the surface pre-treatment of the specimen is of decisive importance [31, 32].

Following are some of the properties of glasses:

i. Glass is transparent but non-crystalline, a major paradox in the physics of condensed matter.

ii. Glass, in general, has a very high resistance to the water and atmospheric agencies.

iii. Glass is hard and yet brittle. When it cracks, it shatters at the speed of sound.

iv. Glass usually breaks in a direction at right angles to the direction of maximum tensile stress.

v. Due to its brittle condition there is no plastic deformation in glass which will break suddenly when subjected to a stress exceeding its elastic limit. Glass obeys Hooke's law accurately until the stress is great enough to cause fracture.

vi. The coefficient of linear thermal expansion is almost constant, for most types of glasses for temperature up to 400-600 °C. The actual value depends on the chemical constitution of the glass.

vii. Glass is electrically insulating at normal temperatures but becomes conducting at elevated temperatures.

All the above and other properties of glasses are infinitely variable and can be tailored according to the particular technological requirement by choosing proper glass composition.

Glass materials have several advantages over crystals in many optical device applications. These advantages include,
1.5 Thermodynamics of glass formation- glass transition

A cooled liquid from high temperature can have two types of pathways, either it may crystallize at or below melting temperature ($T_m$) or it may under cool sufficiently, without nucleation and crystallization to form glass. The cooled liquid taking either of the pathways has been explained incontrovertibly by using Volume-Temperature diagram shown in Fig.1.2. From the figure it could be seen that liquid at high temperature at point ‘$a$’, on cooling, its volume decreases and follows path ‘$abcd$’, typically shown by non-glass forming liquids. The point ‘$b$’ corresponds to melting temperature ($T_m$) and the region ‘$bc$’ represents the crystallisation path. If crystallisation occurs, there will be increase in density at the melting point ($T_m$) and there will be a marked discontinuity in the volume at melting temperature ($T_m$). On further cooling, so formed crystal shrink (volume shrinkage) along path ‘$cd$’. If no crystallisation occurs, liquid on cooling takes the path of ‘$abef$’ or ‘$abgh$’ without any discontinuity in the cooling curve. The region ‘$be$’ represents the liquid is under cooled but does not freeze. With decreasing temperature liquid viscosity increases gradually and the molecules become less mobile and cannot rearrange themselves.
fast enough to reach the volume characteristic of that temperature. Therefore material
acquires rigid without any regular three-dimensional periodicity like crystals. The
change in behaviour or properties from an under cooled liquid to a rigid glass takes
place (shown at point 'e') at temperature or range of temperatures with a change in
their slope called glass transition temperature ($T_g$).

![Diagram of volume-temperature characteristics associated with heating and cooling for crystals and glasses]

Fig. 1.2: Volume-temperature characteristics associated with heating and cooling for crystals and glasses

Glass transition temperature depends upon the rate of cooling of the melt, slower the rate of cooling lower is the value of $T_g$. Thus glass transition temperature $T_g$, is not always the same even if the chemical composition is the same.

A slow cooling rate allows enough time for a viscous liquid to alter the arrangement of local atoms to attain the minimum free energy at this correspondent temperature, where as a rapid cooling causes an increase of viscosity that is too quick for the local atomic arrangements to follow and results in a transition into a glass at a
higher temperature. The structure of a rapidly cooled glass is more open than that of 
a slowly cooled one.

The IUPAC Compendium on Chemical Terminology defines glass transition 
as ‘a second-order transition in which a super cooled melt yields, a glassy structure 
on cooling’. It states that below the glass-transition temperature, the physical 
properties of glasses vary in a manner similar to those of the crystalline phase [33].

1.6 Glass network formers and modifiers

Glasses have been prepared using different types of materials. The ability of a 
substance to form a glass does not depend upon any particular physical or chemical 
property. It is now generally agreed that almost any substance, if cooled sufficiently 
fast could be obtained in the glassy state although in practice crystallization 
intervenes in many substances.

\[ \text{B}_2\text{O}_3, \text{SiO}_2, \text{GeO}_2 \text{ and } \text{P}_2\text{O}_5 \text{ all of which from a certain area of the periodic table readily form glasses on their own, when their melts are cooled and are commonly known as 'glass formers' or 'network formers'. In addition to that, } \text{As}_2\text{O}_3 \text{ and } \text{Sb}_2\text{O}_3 \text{ also produce glass on their own when cooled very rapidly. } \text{TeO}_2, \text{SeO}_2, \text{MoO}_3, \text{WO}_3, \text{Bi}_2\text{O}_3, \text{Al}_2\text{O}_3, \text{Ga}_2\text{O}_3 \text{ and } \text{V}_2\text{O}_5 \text{ will not form glasses on their own, but each will do so when melted with a suitable quantity of certain other non-glass forming oxide. Hence, they are known as 'conditional glass formers' according to Rawson [34].}

\[ \text{Alkali oxides (M}_2\text{O, M}=\text{Li,Na, K, Rb and Cs), alkaline-earth oxides(MO, M}=\text{Mg, Ca, Ba and Sr)} \text{ which when added in small quantities( 10 mol % to 15 mol%) to the network forming oxides produce drastic changes (melting point, conductivity, etc.,) in the properties of the later. Such oxides, also modifies the network structure of the glass and hence they are termed as 'network modifiers' (NWM). The classification of the glass forming oxides is given Table 1.2.} \]
Table 1.2
Glass formers, modifiers and intermediates

<table>
<thead>
<tr>
<th>Glass formers</th>
<th>Modifiers</th>
<th>Intermediates</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>Li₂O</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>GeO₂</td>
<td>Na₂O</td>
<td>Ga₂O₃</td>
</tr>
<tr>
<td>B₂O₃</td>
<td>K₂O</td>
<td>Bi₂O₃</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>CaO</td>
<td>PbO</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>MgO</td>
<td>ZnO</td>
</tr>
<tr>
<td>As₂O₃</td>
<td>BaO</td>
<td>CdO</td>
</tr>
<tr>
<td>Sb₂O₃</td>
<td>SrO</td>
<td>TiO₂</td>
</tr>
</tbody>
</table>

1.7 Classification of glasses

Glasses are classified into different types, based on their chemical compositions, structures and type of bonding [35]. As shown in Table 1.3, materials of every bond type form glasses.

Table 1.3
Classification of glass forming materials based on the bond nature

<table>
<thead>
<tr>
<th>Bond nature</th>
<th>Glass forming materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Covalent</td>
<td>Oxides (silicates, borates, phosphates, germinates, tellurites, etc.), Chalcogenides, organic polymers.</td>
</tr>
<tr>
<td>Ionic</td>
<td>Halides, nitrates, carbonates, sulphates etc.,</td>
</tr>
<tr>
<td>Hydrated ionic</td>
<td>Aqueous solutions of salts</td>
</tr>
<tr>
<td>Molecular</td>
<td>Organic liquids</td>
</tr>
<tr>
<td>Metallic</td>
<td>Spalt-cooled alloys related chemicals</td>
</tr>
</tbody>
</table>
Though there are different types of glasses, since the present study is concerned with the borate glasses, properties of vitreous borate (B$_2$O$_3$) and modifiers and network modifiers are dealt with.

1.8 Vitreous borate (B$_2$O$_3$) and Borate glasses

B$_2$O$_3$ is one of the most common glass former oxides possessing medium range order, used in the preparation of commercially important glasses. It is often used as dielectric and insulating material. Borate glasses are much interest because of the occurrence of boron anomaly. Borate glasses are characterized depending on the properties of the compositions. A number of investigations have earlier been carried out on the structural interpretation of B$_2$O$_3$ beginning with Bray [36], Konijnendijk [37], Krogh-Moe [38] and Tarasova [39].

Vitreous B$_2$O$_3$ structure consists of boroxol rings; each ring consisting of three [BO$_3$] triangles joined together by a common oxygen atom as shown in the Fig.1.3.

![Planar structure of [BO$_3$] triangles in a borate glass](image)

One oxygen atom binding two neighbouring boroxol rings results in the formation of significantly weakened intermolecular bonds between them. In addition, these rings forms planar networks joined by weak Vanderwall’s bonds. Due to the presence of weak bonds between the structural complexes and planar networks, boron oxide has a much lower melting point.
1.8.1 Alkali /Alkaline earth borate glasses

Borate glasses contain a mixture of \([\text{BO}_3]\) triangles and \([\text{BO}_4]\) tetrahedra based on the composition. Addition of modifiers like alkali oxide (\(\text{A}_2\text{O}\)) or alkaline earth oxide (\(\text{AO}\)) to vitreous \(\text{B}_2\text{O}_3\) results with the change in the boron coordination and glass structure, these acts in two ways: i) the conversion of \([\text{BO}_3]\) to \([\text{BO}_4]\) and ii) formation of non-bridging oxygens (NBOs). This peculiar property shown by boron is called as 'Boron anomaly'.

Boron oxide changing from \([\text{BO}_3]\) to \([\text{BO}_4]\) increases the connectivity (i.e., bond strength increases since two \([\text{BO}_4]\) units are joined by a common vertex) and causes thermal expansion to decrease and hence viscosity increases. By varying the modifier concentration in the composition range various cyclic groups like di-, tri-, and penta-borate are formed due to change in the concentration of modifier oxides as shown in the Fig. 1.4 [40].

\[\text{Fig. 1.4: Various structural groups formed in borate glasses}\]
At lower modifier content, $\text{BO}_4$ units are grouped to form tetra-borate units and on increasing the modifier content, $\text{BO}_4$ units associated with di-borate group are formed and on further increasing the content of modifier, $\text{BO}_3$ units with non-bridging oxygens are formed. The order of preference for the bridging oxygen atom configuration between structural units: $B^{31}-O-B^{31} > B^{31}-O-B^{41} > B^{41}-O-B^{41}$.

1.9 Dielectric spectroscopy

Dielectrics are basically insulator materials having a special property of storing and dissipating electric energy when electric field is applied, which gives rise to dielectric phenomenon on interacting with different charged particles. Dielectrics are classified into two classes; they are (i) the polar (high electrical loss materials) and (ii) the non-polar (low electric loss materials). The charge carriers in the dielectric amorphous materials like glasses and polymers etc. cannot move freely through the matrix but instead they are displaced creating dipole field which opposes the applied alternating field and as a response the material gets polarized. Based on the interaction of atoms with the external field, different mechanisms of polarizations are explained here below.

1.9.1 Polarization Mechanisms

The electrical polarization includes four categories that are specified as electronic, ionic (or atomic), dipolar (or orientation), and space charge polarizations, explained as below and shown in Fig. 1.5.

i) **Electronic polarization ($P_e$)**: This arises in neutral atoms when an electric field displaces the nucleus with respect to the electrons that surround it and occurs at the frequencies up to $10^{16}$ Hz.

ii) **Ionic (Atomic) polarization ($P_i$)**: This occurs due to the displacement (or stretch) of negative and positive ions with respect to each other under an applied electric field. This occurs approximately at $10^{13}$ Hz.

iii) **Oriental or Dipolar polarization ($P_d$)**: This is primarily due to change in the orientation of permanent electric dipole moments of molecules governed by the direction of the applied electric field. This occurs at frequencies up to about $10^{10}$ Hz.
iv) Space charge polarization ($P_s$): This is observed in bulk materials containing intrinsic mobile charge carriers (ions/electrons/both) that can migrate a little distance (via diffusion, ionic conduction, hoping and etc.,) due to alignment of dipoles under applied field. Generally this occurs at electrode-electrolyte interfaces. Space charge polarization typically occurs at frequencies between $1$ and $10^3$ Hz.

![Diagram of polarization mechanisms](image)

**Fig. 1.5:** Illustrates the frequency dependence of the electronic, ionic, dipolar, & space charge polarization contributions to the relative dielectric constant and loss.

The total polarization ($P_t$) of the dielectric material can be expressed as the sum of the aforementioned polarizations [41]:

$$P_t = P_e + P_i + P_d + P_s$$  \hspace{1cm} (1.1)

The total polarization $P$ is related to the relative dielectric constant $\varepsilon'$ through the following equation:

$$p = \varepsilon_0 E (\varepsilon' - 1) = \varepsilon_0 \chi E$$  \hspace{1cm} (1.2)

where $\varepsilon_0$ is the permittivity of free space, $\chi$ is the electric susceptibility and $E$ is the applied ac electric field.
1.9.2 Dielectric properties

When a dielectric material is introduced in an a.c. electric field there will be phase lag between the applied field and the response of the system. This is due to losses associated with the presence of polarisable entities in the dielectric or due to inertial effects [42].

1.9.2 (a) Dielectric constant (\( \varepsilon' \)) and loss tangent (\( \tan \delta \))

According to Debye's model, the complex permittivity of the system is calculated using the impedance data:

\[
\varepsilon^* = \varepsilon_{\infty} + \frac{\varepsilon_s - \varepsilon_{\infty}}{1 + i\omega \tau}
\]

(1.3)

where \( \varepsilon_s \) is the static dielectric constant, \( \varepsilon_{\infty} \) is the dielectric constant value of the material corresponding to its electronic and atomic polarization, \( \tau \) is the relaxation time and \( \omega \) is the angular frequency. On writing the equation in terms of \( \varepsilon' \) and \( \varepsilon'' \) we get the following equations:

\[
\varepsilon'(\omega) = \frac{\varepsilon_s - \varepsilon_{\infty}}{1 + \omega^2 \tau^2}
\]

(1.4) and

\[
\varepsilon''(\omega) = \frac{(\varepsilon_s - \varepsilon_{\infty}) \omega \tau}{1 + \omega^2 \tau^2}
\]

(1.5)

The real part of permittivity (dielectric constant) \( \varepsilon' \) represents the polarizability of the material (or energy stored in a material), while the imaginary part (dielectric loss) \( \varepsilon'' \) represents the energy loss due to polarization and ionic conduction. Dielectric loss-tangent (\( \tan \delta \)), represents tangent of the angle between displacement phasor and total current, it is given by:

\[
\tan \delta = \frac{\varepsilon''}{\varepsilon'} = \frac{(\varepsilon_s - \varepsilon_{\infty}) \omega \tau}{\varepsilon_s - \varepsilon_{\infty} \omega^2 \tau^2}
\]

(1.6)

1.9.2 (b) A.C conductivity analysis

The frequency dependent mechanism for the present glass system is analyzed on the basis of Jonscher universal power law [43]

\[
\sigma(\omega) = \sigma_0 + A \omega^s \quad 0 < s < 1
\]

(1.7)
where $\sigma_{dc}$ is the dc conductivity, $A\left(=\frac{\sigma_{dc}}{\omega^s}\right)$ is temperature dependent constant, $\omega=2\pi f$ is the angular frequency of the applied field and $s$ is the power law exponent in the range $0<s<1$, represents the degree of interaction between the mobile ions. It can be measured by taking slope of $\log \sigma(\omega)$ versus $\log \omega$ for the curves. The frequency dependence of conductivity is sum of the dc conductivity due to movements of free charges and polarization conductivity (ac conductivity) due to movements of bound charges. In the high frequency region, conductivity become strongly frequency dependent, and exhibits linear behaviour which follows a power law relation:

$$\sigma(\omega) = A\omega^s \quad s < 1$$ (1.8)

Therefore, the conductivity increases with increase of the frequency. The exponent $s$ value is obtained from the equation $S = \frac{d\left(\ln \sigma(\omega)\right)}{d\left(\ln(\omega)\right)}$ at room temperature.

1.10 Optical absorption spectroscopy

Optical absorption spectroscopy is a powerful tool by means of which the nature of the surroundings around the dopant ions (rare-earth/transition metals) and the degree of covalence of the metal-ligand bond in a material can be analyzed. The absorption spectra of transition metal ions are influenced by the nature of the host matrices into which those ions are accommodated owing to the excitation spectra of 3d electrons. The absorption spectra of transition metals are fairly broader and are sensitive to the changes in coordination and symmetry. Due to the presence of various oxidation states, each of the states can give rise to different absorption spectra which can be explained by the application of ligand field theory.

1.10.1 Transition metal ions

The elements ranging from $3d^24s^2$ (Ti) to $3d^{10}4s^1$ (Cu) are considered transition metals. Transition metal ions in which the 3d electron levels are incomplete and contain 1-9 of the 10 possible electrons ($Ti^{3+}$ - Cu$^{2+}$ ions) can be used as dopant ions in glassy materials. Many crystals/glasses containing transition metal
from any then known". Manganese is the 12th most abundant element and 3rd most abundant transition metal, exceeded only by iron and titanium, reaching an overall abundance of 0.106% in the earth’s crust. Several silicates, oxides and carbonates containing Manganese are of economical importance, such as hausmannite (Mn2O4), rhodochrosite (MnCO3), manganite (Mn2O3H2O), and pyrolusite (MnO2), while the latter probably has been used for glass fabrication already since the ancient times of the Pharaohs. Generally, Manganese is moderately reactive. At higher temperature, it reacts vigorously with oxygen, nitrogen, chlorine and fluorine, and combines directly with B, C, Si, P, As, and S. Due to its formidable range of oxidation states, oxides are known based on Mn2+ to Mn7+. 

The Mn2+ ion has an emission which consists of a broad band, the position of which depends strongly on the host lattice. The emission can vary from green to deep red. The decay time of this emission is of the order of ms. From the Tanabe-Sugano diagram it is derived that the emission corresponds to the 4T1→ 6A1 transition. This explains all the spectral properties: a broad band due to different slopes of the energy levels, a long decay time due to the spin selection rule, and a dependence of the emission color on the host lattice due to the dependence on crystal field. Tetrahedrally co-ordinated Mn2+ (weak crystal-field) usually gives a green emission, octahedrally coordinated Mn2+ (stronger crystal field) give an orange to red emission. Mn2+ is an efficient green phosphor widely used in plasma display panels (PDPs), cathode ray tube (CRT), tri-color lamps, color television and thin film electroluminescent devices because of its high luminescence efficiency, the purity of color, chemical stability and large color gamut. Mn2+ doped luminescent materials have been known to have wide-range emissions from 500 to 700 nm depending on the crystal field of the host materials.

1.10.1 (b) Cobalt

Cobalt is a hard, lustrous, grey metal, a chemical element with symbol Co and atomic number 27. Although cobalt-based colors and pigments have been used since ancient times for making jewelry and paints, and miners have long used the name kobold ore for some minerals, the free metallic cobalt was not prepared and
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