CHAPTER-V

ELECTRICAL CONDUCTIVITY OF TUNGSTATE COMPOUNDS AT HIGH TEMPERATURE

5.1 INTRODUCTION

To determine the electrical conduction mechanism in a material which conducts very little conductivity is a very difficult task. In general, one has to find out first whether the conduction is electronic or ionic or mixed (both ionic and electronic) then to determine the source of ionic conduction (anion or cation vacancies or interstitial etc.) or the electronic conduction (intrinsic or extrinsic). After this has been decided one has to find out the mechanism of conduction and evaluate various parameters like number (n), activation energy (E_a) and mobility (μ) of charge carriers using appropriate models. To have good quantitative idea of above mentioned parameters, one needs several types of experimental data, e.g. electrical conductivity (σ) as a function of time, electric field, ac signal frequency, temperature and doping, dielectric constant (K’) and loss (K’’) as a function of frequency and temperature etc. It is not easy to obtain all these data in any single laboratory. A quantitative understanding and semi qualitative analysis of the conduction mechanism can be presented by studying the electrical conductivity as a function of various parameters (Dwivedi et al. 2001, Aung et al. 2005, Hirota et al. 2003). In general electrical conductivity gives mixed information about number and mobility of charge carriers. The study of electrical conductivity yield some important information about
conduction process in any solid. Using this methodology we have investigate electrical transport mechanism of tungstate compounds and details are presented in this chapter.

5.2 MATERIAL PREPARATION AND EXPERIMENTAL PROCEDURE

The tungstate compounds of formula Ce$_2$(WO$_4$)$_3$, TbWO$_4$, Dy$_2$(WO$_4$)$_3$, Ho$_2$(WO$_4$)$_3$, Er$_2$(WO$_4$)$_3$, Yb$_2$(WO$_4$)$_3$ were prepared by using procedure described in chapter IV and characterised by X-ray diffraction techniques. The main measurement done is electrical conductivity for the electrical transport study. The details about the procedure adopted and apparatus used are given in chapter III. The electrical conductivity measurement was performed on pressed pellets because of the difficulty in growing large single crystals of these compounds needed for such measurements due to their high melting point and our limited facilities. In pellets grain boundaries and air pores considerably reduce $\sigma$ values and often measurements on them do not reflect the bulk value for the material. It is not possible to eliminate them completely; however pellets can be prepared in such a way that these effects are considerably reduced. In such a situation the bulk value for the material can be obtained employing suitable corrections. The first requirement in this direction is to make pellets of uniform density. This has been achieved by using a proper steel die and keeping $t^2/A$ (Where $t$ is the thickness and $A$ the face area of the pellet) ratio less than 0.4 fixed by other workers (Kumar 1971, Tripathi 1981, Tripathi and Lal 1982 and Lal et al. 1982). The details are described in chapter IV.
5.3 STUDY OF PELLET DENSITY AND ELECTRICAL CONDUCTIVITY AS A FUNCTION OF PELLETIZING PRESSURE

The densities of pellets of each studied compound well annealed at appropriate temperature have been obtained from the measurement of its volume and mass. The mass of each compound is obtained by weighing the pellets on a sensitive balance. The thickness and area of the pellets are taken out and thereby the density of the pellets is calculated. The density measurement has been done on each pellet of the compound made at a pressure ranging from $3.04 \times 10^8$ to $8.4 \times 10^8$ Nm$^{-2}$. The variation of pellet density ($d_p$) with pelletizing pressure (P) is shown in Fig. 5.1 for different compounds. It is seen from these figures that the pellet density ($d_p$) depends upon the pelletizing pressure. It increases almost linearly till P equals $4.96 \times 10^8$ Nm$^{-2}$ and after that the increase becomes slow and when p exceeds $7.04 \times 10^8$ Nm$^{-2}$, the density becomes almost constant. The maximum density of the pressed pellets, however, remains less than the reported X-ray density ($d_0$) for the materials. Thus pore exist in the pressed pellets. The pore fraction ($f_p$) for highest pressed pellet is determined using the relation

$$f_p = \frac{d_0 - d_p}{d_0}$$  \hspace{1cm} (5.1)

The values of $d_0$, $d_p$ and $f_p$ for all the studied compounds are given in Table 5.1. The pore fraction is so small that the bulk value of any parameter can be obtained using suitable corrections. The electrical conductivity ($\sigma_p$) of several pellets of each compound made at different pelletizing pressures (P) were measured using silver foil electrodes at a fixed temperature. The plots of $\log\sigma_p$ vs P for different compounds are given in Fig. 5.2. It is seen from this figure that $\log\sigma_p$ depends upon
TABLE-5.1

THE X-RAY DENSITY (d₀), PELLET DENSITY (dₚ) OF HIGHEST PRESSED PELLET AND PORE FRACTION (fₚ) FOR STUDIED COMPOUNDS

<table>
<thead>
<tr>
<th>Compounds</th>
<th>d₀×10⁻³ (Kgm⁻³)</th>
<th>dₚ×10⁻³ (Kgm⁻³)</th>
<th>fₚ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce₂(WO₄)₃</td>
<td>3.274</td>
<td>3.182</td>
<td>0.028</td>
</tr>
<tr>
<td>TbWO₄</td>
<td>3.298</td>
<td>3.200</td>
<td>0.030</td>
</tr>
<tr>
<td>Dy₂(WO₄)₃</td>
<td>3.591</td>
<td>3.571</td>
<td>0.006</td>
</tr>
<tr>
<td>Ho₂(WO₄)₃</td>
<td>4.994</td>
<td>4.691</td>
<td>0.061</td>
</tr>
<tr>
<td>Er₂(WO₄)₃</td>
<td>5.063</td>
<td>4.983</td>
<td>0.016</td>
</tr>
<tr>
<td>Yb₂(WO₄)₃</td>
<td>5.669</td>
<td>5.446</td>
<td>0.039</td>
</tr>
</tbody>
</table>

pressures. It increases with P and tends to become constant when P exceeds 6.75×10⁸ Nm⁻². The relatively low conductivity observed at lower pressure is obviously due to presence of less conducting grain boundary regions. These and likewise effects decrease to some extent when pelletizing pressure is increased. This fact is strengthened further by the observed constancy in the density of the pellets at higher pelletizing pressures σₚ of pellets made at same P having different dimensions are practically same. No effect of pellet shape and size has been observed on σₚ. It has been generally observed that both conductivity and density of the pellets attain their maximum value at the same pelletizing pressure. Though the constancy observed in dₚ and σₚ
FIG. 5.1 PLOTS OF PELLET DENSITY ($d_p$) AGAINST PELLETIZING PRESSURE ($P$)
ensures significant reduction of grain boundary effect yet the density of the pellet lesser than the X-ray density of the material indicates that $\sigma_p$ may be significantly smaller than the crystalline value of electrical conductivity ($\sigma$). The estimation of $\sigma$ from $\sigma_p$ has been done by a standard relation (Russel 1935).

$$\sigma = \sigma_p \left\{ 1 + \frac{f}{1 + f^2} \right\}$$

(5.2)

5.4 STUDY OF CURRENT DENSITY AS A FUNCTION OF APPLIED ELECTRIC FIELD

The role of the electrode in the measurement of electrical conductivity ($\sigma$) is very important. For such measurement it is essential that the contact between the pellet and electrode interface is ohmic (Roberts 1968). Even in the case of the ohmic contact, the contact resistance play an important role in the measurement of $\sigma$ for high conducting solids. However, they are relatively less important in the case of low conducting solids. To ensure the ohmic contact between the pellet and electrode interface, the current through the pellet has been measured at different applied voltages at constant temperature. Both current through and voltage across the pellet have been measured using Keithley digital multimeter type 171. Using dimension of the pellet, the current density ($J$) and electric field ($E$) have been evaluated. The results for different compounds are shown in Fig.5.3. It is seen from this figure that except at very low fields, $J$ vs $E$ plots are linear. This ensures ohmic contact between pellet and electrode interface. In all further
measurements we have used well sintered pellets made at higher pelletizing pressures and electric field (E) in the range where contact between electrode and pellet interface was ohmic.

FIG. 5.2 PLOTS OF LOGARITHMS OF ELECTRICAL CONDUCTIVITY OF PELLETS (Log σ_p) AGAINST PELLETIZING PRESSURE (P) AT CONSTANT TEMPERATURE (T = 770K)
FIG. 5.3 PLOTS OF CURRENT DENSITY (J) AGAINST ELECTRIC FIELD (E) AT CONSTANT TEMPERATURE
5.5 STUDY OF ELECTRICAL CONDUCTIVITY AS A FUNCTION OF FREQUENCY AND TIME

The experimental work carried out by several workers (Bogoroditskil et al. 1965, Bosman and Van-Daal 1970, Subbarao et al. 1970, Naito et al. 1974 etc.) both on pressed pellets and single crystals of same material have clearly demonstrated the effect of grain boundaries. Various superfluous effects, not at all connected with the bulk properties of the crystals, can arise purely due to grain boundaries. The grain boundary effects in pellet are reduced if fine and uniform powders are taken for making pellets and sintered at higher temperature for significantly long time. In any case, if sintered pellets are used for conductivity measurements then it is necessary to ensure that grain boundaries effects are negligible. This can be demonstrated by measuring $\sigma$ at various frequencies and showing that it does not depend appreciably on it. To show that grain boundary effects are minimised, the electrical conductivity of some highly pressed pellets of each compounds have been measured at different ac signal frequencies at a constant temperature. The overall error in conductivity measurement were less than two percent. The frequencies of measurement are 100Hz, 1KHz. The plot of $\log\sigma$ as a function of logarithm of ac signal frequency for all compounds are shown in Fig.5.4. It is seen from these figures that conductivity is nearly independent of frequency. This indicates that grain boundary effects are sufficiently minimised for highly pressed pellets. The dc values of electrical conductivity are also given in these figures. They are almost same as ac conductivity at that temperature.
Current density through the tungstate compounds have been measured with time at constant temperature. The applied field was in the range corresponding to ohmic contact. The results obtained are shown in Fig.5.5. It is observed from these figures that the current is independent of time. From these observations we conclude that there is no ionic conductivity in studied compounds.
Ce$_2$(WO$_4$)$_3$  $T = 862K$  $E = 1.3 \times 10^3 (\text{vm}^{-1})$

TbWO$_4$  $T = 909K$  $E = 2.1 \times 10^3 (\text{vm}^{-1})$

Dy$_2$(WO$_4$)$_3$  $T = 714K$  $E = 2.2 \times 10^3 (\text{vm}^{-1})$

Ho$_2$(WO$_4$)$_3$  $T = 960K$  $E = 3.1 \times 10^3 (\text{vm}^{-1})$

Er$_2$(WO$_4$)$_3$  $T = 1042K$  $E = 1.20 \times 10^3 (\text{vm}^{-1})$

Yb$_2$(WO$_4$)$_3$  $T = 625K$  $E = 5.12 \times 10^3 (\text{vm}^{-1})$

FIG. 5.5 PLOTS OF CURRENT DENSITY ($J$) AGAINST TIME ($t$) AT CONSTANT TEMPERATURE AND FIELD
5.6 STUDY OF AC ELECTRICAL CONDUCTIVITY AS A FUNCTION OF TEMPERATURE

The measurement of electrical conductivity of few pellets of tungstate compounds have been carried out in air in temperature range 303K to 1103K. The measurements have been done on pellets made at P>6.8 × 10^8 Nm^{-2} and sintered at 1200K for 50 hrs. The conductivity values for a particular compound do not differ from sample to sample. It is also independent of pellet thickness. Further for each pellet no significant difference have been observed in conductivity values during heating and cooling cycles. It also remains almost same irrespective of thermal history or self life of the pellet. The mean value of conductivity for few pellets of each compound has been taken as bulk conductivity of pressed pellets. The crystalline value of electrical conductivity (σ) has been calculated using relation 5.2. The variation of log σ with inverse of absolute temperature (T^{-1}) for different compounds are shown in Figs. 5.6 to 5.11. It is seen from these figures that σ values for these compounds are between 10^{-6} to 10^{-3} Ω^{-1}m^{-1} in the temperature range 303-1103K. It is seen from the figures that each plot can be divided into two linear ranges except Ce₂(WO₄)₃ and Yb₂(WO₄)₃ which have three ranges namely range I lying between T<T₁, range II, T₁<T<T₂ and range III for
The temperature $T_1$ and $T_2$ are termed as phase transition and break temperature respectively and are listed in table 5.3 for studied compounds.

The linear region of $\log \sigma$ vs $T^{-1}$ plot can be represented by the usual relation

$$\sigma = \sigma_0 \exp \left( \frac{-E_a}{kT} \right)$$

(5.3)

The values of pre-exponential constant ($\sigma_0$) and activation energy ($E_a$) have been evaluated from the experimental plot and are also given in Table 5.2 to 5.4.

### TABLE-5.2

CONSTANTS OF THE LINEAR RANGE $T<T_1$ IN $\log \sigma$ vs $T^{-1}$ PLOTS AND TEMPERATURE $T_1$ FOR STUDIED COMPOUNDS

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T_1$</th>
<th>$\sigma_0$</th>
<th>$E_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ce}_2(\text{WO}_4)_3$</td>
<td>583</td>
<td>$4.75\times10^{-5}$</td>
<td>0.09</td>
</tr>
<tr>
<td>$\text{TbWO}_4$</td>
<td>699</td>
<td>$5.84\times10^{-5}$</td>
<td>0.10</td>
</tr>
<tr>
<td>$\text{Dy}_2(\text{WO}_4)_3$</td>
<td>588</td>
<td>$2.94\times10^{-4}$</td>
<td>0.10</td>
</tr>
<tr>
<td>$\text{Ho}_2(\text{WO}_4)_3$</td>
<td>763</td>
<td>$6.37\times10^{-5}$</td>
<td>0.10</td>
</tr>
<tr>
<td>$\text{Er}_2(\text{WO}_4)_3$</td>
<td>794</td>
<td>$1.00\times10^{-4}$</td>
<td>0.10</td>
</tr>
<tr>
<td>$\text{Yb}_2(\text{WO}_4)_3$</td>
<td>505</td>
<td>$1.48\times10^{-4}$</td>
<td>0.10</td>
</tr>
</tbody>
</table>
FIG. 5.6 PLOTS OF LOGARITHM OF ELECTRICAL CONDUCTIVITY (Log $\sigma$) AGAINST INVERSE OF ABSOLUTE TEMPERATURE ($T^{-1}$)
FIG. 5.7 PLOTS OF LOGARITHM OF ELECTRICAL CONDUCTIVITY (Log $\sigma$) AGAINST INVERSE OF ABSOLUTE TEMPERATURE ($T^{-1}$)
FIG. 5.8 PLOTS OF LOGARITHM OF ELECTRICAL CONDUCTIVITY (Log $\sigma$) AGAINST INVERSE OF ABSOLUTE TEMPERATURE ($T^{-1}$)
**FIG. 5.9**  PLOTS OF LOGARITHM OF ELECTRICAL CONDUCTIVITY (Log $\sigma$) AGAINST INVERSE OF ABSOLUTE TEMPERATURE ($T^{-1}$)
FIG. 5.10 PLOTS OF LOGARITHM OF ELECTRICAL CONDUCTIVITY (Log $\sigma$) AGAINST INVERSE OF ABSOLUTE TEMPERATURE ($T^{-1}$)
FIG. 5.11 PLOTS OF LOGARITHM OF ELECTRICAL CONDUCTIVITY (Log $\sigma$) AGAINST INVERSE OF ABSOLUTE TEMPERATURE ($T^{-1}$)
### TABLE-5.3

**CONSTANTS OF THE LINEAR RANGE T_1<T<T_2 IN Logσ vs T⁻¹ PLOTS AND TEMPERATURE T_1 AND T_2 FOR STUDIED COMPOUNDS**

<table>
<thead>
<tr>
<th>Compound</th>
<th>T_1 (K)</th>
<th>σ₀ (Ω⁻¹m⁻¹)</th>
<th>E_a (eV)</th>
<th>T_2 (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce₂(WO₄)₃</td>
<td>583</td>
<td>3.75×10⁹</td>
<td>2.02</td>
<td>794</td>
</tr>
<tr>
<td>TbWO₄</td>
<td>699</td>
<td>7.42×10²</td>
<td>2.98</td>
<td>-</td>
</tr>
<tr>
<td>Dy₂(WO₄)₃</td>
<td>588</td>
<td>8.88×10⁷</td>
<td>1.76</td>
<td>-</td>
</tr>
<tr>
<td>Ho₂(WO₄)₃</td>
<td>763</td>
<td>1.12×10⁹</td>
<td>2.57</td>
<td>-</td>
</tr>
<tr>
<td>Er₂(WO₄)₃</td>
<td>794</td>
<td>8.40×10¹³</td>
<td>3.47</td>
<td>-</td>
</tr>
<tr>
<td>Yb₂(WO₄)₃</td>
<td>505</td>
<td>7.44×10²</td>
<td>0.92</td>
<td>781</td>
</tr>
</tbody>
</table>

### TABLE-5.4

**CONSTANTS OF THE LINEAR RANGE T>T_2 IN Logσ vs T⁻¹ PLOTS AND TEMPERATURE T_2 FOR STUDIED COMPOUNDS**

<table>
<thead>
<tr>
<th>Compound</th>
<th>T_2 (K)</th>
<th>σ₀ (Ω⁻¹m⁻¹)</th>
<th>E_a (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce₂(WO₄)₃</td>
<td>794</td>
<td>1.87×10¹³</td>
<td>3.25</td>
</tr>
<tr>
<td>Yb₂(WO₄)₃</td>
<td>781</td>
<td>1.22×10⁶</td>
<td>1.68</td>
</tr>
</tbody>
</table>
5.7 DISCUSSION

The variation of electrical conductivity as a function of various parameters have been presented in preceding sections. One of these results is the variation of dc electrical conductivity with time. It has been found independent of time even at relatively higher current and sufficiently long time. Also no significant difference has been observed between dc and ac values of electrical conductivity at any temperature. Further, ac conductivity has been found independent of signal frequencies. All these observations indicates that tungstate compounds are essentially electronic conductors and ionic conductivity if any, is significantly small. Thus majority charge carriers in these solids are either electrons or holes. Around 300K electrical conductivity of studied compounds is of the order of $10^{-6} \, \Omega^{-1}\text{m}^{-1}$ and increases with the increase of temperature. Hence at normal temperature the studied compounds are typical semiconducting solids. The conductivity is highest for Dy$_2$(WO$_4$)$_3$ and lowest for Ce$_2$(WO$_4$)$_3$. Log$\sigma$ vs T$^{-1}$ plots for the studied compounds have two linear regions except Ce$_2$(WO$_4$)$_3$ and Yb$_2$(WO$_4$)$_3$ which have three linear regions. One lying below $T_1$, other between $T_1$ and $T_2$ and third above $T_2$. The slope of log$\sigma$ vs T$^{-1}$ plots for the first temperature range is small (~0.1 eV) for all the studied compounds. The pre-exponential constant ($\sigma_0$) for all the studied compounds in this temperature range are also small (~$10^{-5}$–$10^{-4} \, \Omega^{-1}\text{m}^{-1}$). Both these values are not appropriate for intrinsic conduction. Thus at temperature T$<T_1$ the electrical conductivity in these compounds seems to be extrinsic. Above $T_1$ the values of activation energy as well as the pre-exponential constant of the studied compounds are large. Hence above $T_1$ the
electrical conduction seems to be intrinsic. The electrical conduction below $T_1$ in all studied compounds are due to impurities or defects. Thus in order to explain the electrical conduction one has to look possible defects and impurities in these materials. Chemical impurities in these compounds are also expected. Thus formation of defect centres either due to non-stoichiometry or chemical defect are quite probable. The charge carriers from these centres may be thermally excited to respective bands and conduct via band mechanism or they may be localised and may conduct via hopping mechanism.

A small dip is observed in the curves around the temperature of 583K for $\text{Ce}_2(\text{WO}_4)_3$, 699K for $\text{TbWO}_4$, 588K for $\text{DY}_2(\text{WO}_4)_3$, 763K for $\text{Ho}_2(\text{WO}_4)_3$, 794K for $\text{Er}_2(\text{WO}_4)_3$ and 505K for $\text{Yb}_2(\text{WO}_4)_3$. This probably reflects phase transition temperature of the solid (Nassau et al. 1965).

At higher temperature ($T>T_1$) the log$\sigma$ vs $T^{-1}$ curve is almost linear and can be expressed by the following expression

$$\sigma = \sigma_0 \exp\left(-\frac{E_g}{2kT}\right)$$

(5.4)

This type of conductivity result are common for electrons or holes and for large polarons. However this result can easily be written in the form

$$\sigma = \sigma_0 \exp\left\{-\left(\frac{1}{T}\right) - \left(\frac{E_g}{2kT}\right)\right\}$$

(5.5)

where $\hbar$ is the Debye temperature and $E_g$ is the band gap of the solid, which is the expression of the $\sigma$ for intermediate polarons. A little temperature dependence of the pre-exponential factor is not ruled out. In particular the data are consistent with a variation of the form
\[ \sigma = AT^{-\frac{1}{2}} \exp\left( -\frac{E_u}{kT} \right) \]

Such an equation is appropriate for the conduction of thermally activated hopping of small polaron at high temperature. The conduction band 5d is also expected to be narrow in these solids. This together with the fact that the lattice is ionic and highly polarizable suggests that the charge carriers will be polarons as discussed by so many authors in 3d and 4f compounds (1954, Allcock 1956, Klinger 1965, 68, Appel 1968, 70 and Sumi 1972). In any case polaron is more general and may include electron or hole type of conduction in extreme limit of very weak coupling.

5.8 CONCLUSION

On the basis of above studies following conclusions can be drawn about electrical conduction of studied compounds.

1. These are semiconducting materials with a electrical conductivity value of the order of $10^{-6} \ \Omega^{-1} \text{m}^{-1}$ around 300K which becomes of the order of $10^{-4} \ \Omega^{-1} \text{m}^{-1}$ to $10^{-3} \ \Omega^{-1} \text{m}^{-1}$ around 1103K. The maximum conductivity is observed for Dy$_2$(WO$_4$)$_3$ and lowest for Ce$_2$(WO$_4$)$_3$.

2. log\(\sigma\) vs T$^{-1}$ plots for the studied compounds have two linear regions. Except Ce$_2$(WO$_4$)$_3$ and Yb$_2$(WO$_4$)$_3$ which have three linear regions. First below T<T$_1$, second between T$_1$<T<T$_2$ and third above T>T$_2$.

3. The electrical conduction below T$_1$ is essentially extrinsic. In the second and third ranges conduction is essentially intrinsic. The charge carriers are polarons at T>T$_1$. The activation energy in third range increases in Ce$_2$(WO$_4$)$_3$ and Yb$_2$(WO$_4$)$_3$.

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CHAPTER-VI

DIELECTRIC PROPERTIES OF TUNGSTATE COMPOUNDS

6.1 INTRODUCTION

The dielectric characteristic of solid materials are of increasing importance due to their various applications in the field of solid state electronics. The principal applications of ceramic dielectrics are as capacitive elements in electronic circuits and as electrical insulator. For these applications we are mainly concerned with some properties of dielectrics such as the dielectric constant and dielectric loss.

In search of new materials for device applications observed that in spite of some structural and compositional similarities of different numbers of an oxides family, they have interesting structural and physical properties (Bera and Choudhary 1995, Okuyama and Hamakawa 1991). Ferroelastic behaviour of the compound can be found in number of papers (Aizu 1969). A detail studies of dielectric and other ferroelectric properties of lead molybdate and lead tungstate have also been reported (Bues et al. 1956, Clark and Doyle 1966). Among them some tungstates and molybdates of different structural families have been found interesting because of their low dielectric constant and high dielectric loss (Moulson and Herbert 1985, Bera and Choudhary 1986). The tungstate compounds Ce$_2$(WO$_4$)$_3$, TbWO$_4$, Dy$_2$(WO$_4$)$_3$, Ho$_2$(WO$_4$)$_3$, Er$_2$(WO$_4$)$_3$, Yb$_2$(WO$_4$)$_3$ are orthorhombic unit cell at room temperature. The dielectric studies are reported in this chapter.
6.2 MATERIAL PREPARATION AND EXPERIMENTAL TECHNIQUE

Tungstate compounds in powder form were prepared using appropriate oxides of tungsten and rare-earth elements employing solid state reaction with one intermediate grinding and firing as described in chapter IV. Pressed pellets have been used for the measurement of dielectric constant and loss. The preparation of uniform density pellets have been described in chapter IV. These pellets were sintered around 1200K about 50 hrs. The details of cleaning and electrode making have also been described in chapter IV. Two electrode method has been used for the measurement of dielectric constant and loss. The pellet with electrodes on its two faces was put on the rigid electrode of the sample holder. The loaded sample holder was then put in a furnace. The capacitance and Q factor of the sample have been measured using auto LCR-Q tester (SYSTRONICS-928, India). The temperature of the sample inside the furnace was raised by a rectangular furnace which automatically records the temperature with chromel-alumel thermocouple fitted inside it.

6.3 DIELECTRIC CONSTANT AND LOSS STUDIES

The measurement of capacitance (C) and quality factor (Q) of pressed and sintered pellets of the studied tungstate compounds have been done at different temperature using two electrode method. The measurements have been done in both heating and cooling cycles but no significant difference has been observed in these values. In measuring the quality factor (Q), the pellet of studied material has been as equivalent to pure capacitor with a high resistance in parallel, which
however, is the internal arrangement of the ‘Q’ meter. The dielectric constant \( (K') \) and dielectric loss \( (K'') \) of the material have been determined using the following formula,

\[
K' = \frac{tc}{A \varepsilon_0}
\]

and

\[
K'' = \frac{K'}{Q}
\]

where \( t \) and \( A \) are the thickness and face area of the pellet respectively and \( \varepsilon_0 \) is the permittivity of the vacuum or free space.

The variation of \( \log K' \) and \( \log K'' \) is shown in Figs. 6.1 to 6.6 for \( \text{Ce}_2(\text{WO}_4)_3 \), \( \text{TbWO}_4 \), \( \text{Dy}_2(\text{WO}_4)_3 \), \( \text{Ho}_2(\text{WO}_4)_3 \), \( \text{Er}_2(\text{WO}_4)_3 \) and \( \text{Yb}_2(\text{WO}_4)_3 \) respectively. It is seen from these figures that the tungstate compounds have high dielectric constant from 25 to 159 for all at 400K. Since dielectric constant \( (K') \) seems to have almost no temperature dependance. These values may be taken as the room temperature values of the materials. The reported value of \( K' \) has been calculated using the capacitance value for the pressed pellets. The density of these pellets remains less than the theoretical density reported for these materials. This means pellets contain air pores. Therefore a correction for pore fraction \( (f_p) \) is essential to obtain the bulk value of the dielectric constant \( (K'_b) \).

\[
f_p = \frac{d_0 - d_p}{d_0}
\]

For low conducting solids \( K'_b \) is related to \( K' \) and \( f_p \) by the following relation (Loyen 1965)
This relation can be used for all the studied tungstate compounds upto 400K because up to this temperature $\sigma$ values are small. The evaluated values of $K'_b$ are shown in Table 6.1.

**TABLE-6.1**

**THE BULK VALUE OF DIELECTRIC CONSTANT ($K'_b$) OF THE STUDIED COMPOUNDS AT 400 K**

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Ce$_2$(WO$_4$)$_3$</th>
<th>TbWO$_4$</th>
<th>Dy$_2$(WO$_4$)$_3$</th>
<th>Ho$_2$(WO$_4$)$_3$</th>
<th>Er$_2$(WO$_4$)$_3$</th>
<th>Yb$_2$(WO$_4$)$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K'_b$ at 400K</td>
<td>40.2</td>
<td>161.2</td>
<td>100.2</td>
<td>32.2</td>
<td>24.9</td>
<td>24.9</td>
</tr>
</tbody>
</table>

The values of dielectric constant ($K'$) of all these materials become large as temperature is increased and validity of Eq. 6.4 becomes doubtful. Further this formula change only the magnitude of $K'_b$ but not the temperature variation of $K'$, therefore we have not used this correction at higher temperature and have used the $K'$ values evaluated from the capacitance measurement of pressed pellets.

We have measured the dielectric constant and dielectric loss of all the tungstate compounds at frequency 1KHz as a function of temperature. The value of dielectric constant and dielectric loss of all the studied compounds at temperature 400K, 600K, 800K and 1000K at the frequency 1KHz are given in Table 6.2 and 6.3 respectively.
TABLE-6.2

THE DIELECTRIC CONSTANT (K') FOR THE STUDIED TUNGSTATE COMPOUNDS AT DIFFERENT TEMPERATURES MEASURED AT 1 kHz

<table>
<thead>
<tr>
<th>Compounds</th>
<th>400K</th>
<th>600K</th>
<th>800K</th>
<th>1000K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce$_2$(WO$_4$)$_3$</td>
<td>40</td>
<td>100</td>
<td>3.16×10$^3$</td>
<td>1.00×10$^5$</td>
</tr>
<tr>
<td>TbWO$_4$</td>
<td>159</td>
<td>398</td>
<td>2.51×10$^3$</td>
<td>7.94×10$^4$</td>
</tr>
<tr>
<td>Dy$_2$(WO$_4$)$_3$</td>
<td>100</td>
<td>159</td>
<td>5.01×10$^2$</td>
<td>2.51×10$^3$</td>
</tr>
<tr>
<td>Ho$_2$(WO$_4$)$_3$</td>
<td>32</td>
<td>40</td>
<td>1.00×10$^2$</td>
<td>1.00×10$^4$</td>
</tr>
<tr>
<td>Er$_2$(WO$_4$)$_3$</td>
<td>25</td>
<td>32</td>
<td>7.94×10$^1$</td>
<td>3.98×10$^3$</td>
</tr>
<tr>
<td>Yb$_2$(WO$_4$)$_3$</td>
<td>25</td>
<td>100</td>
<td>5.01×10$^2$</td>
<td>1.26×10$^4$</td>
</tr>
</tbody>
</table>

It is seen from the table 6.2 that

(i) The highest dielectric constant at 400K is that of TbWO$_4$.

(ii) The dielectric constant has a very slow increase with a temperature at least up to 500K.

The limit of constancy of K' goes up to 583K for Ce$_2$(WO$_4$)$_3$, 700K for TbWO$_4$, 600K for Dy$_2$(WO$_4$)$_3$, 763K for Ho$_2$(WO$_4$)$_3$, 795K for and 775K for Yb$_2$(WO$_4$)$_3$. The small increase in K' is in accordance with usual trend for ionic solids (Smyth 1955, Srivastava and Varshney 1956 and Chandra 1969). This happens because lattice expands and polarizability of the constituents ions are affected by change in temperature and available volume. The systematic trend of K' variation reveals that polarization mechanism in all the compounds is same. A
relatively larger value of $K'$ in case of $\text{Ce}_2\text{(WO}_4\text{)}_3$ appears due to the presence of impurities which forms some kind of donor centres and have larger polarizability. The dielectric constant has a very slow increase at lower temperature. Generally for any solid, the contribution to $K'$ is made by the following factors:

(i) The electronic polarizability of constituent.
(ii) Atomic (or ionic) polarizability of the lattice.
(iii) Orientational polarizability of dipoles
(iv) Space charge polarizability of thermally generated charge carriers. This arise when some group of charges are held some where in the solid.

TABLE-6.3
THE DIELECTRIC LOSS ($K'$) FOR THE STUDIED TUNGSTATE COMPOUNDS AT DIFFERENT TEMPERATURES MEASURED AT 1 kHz

<table>
<thead>
<tr>
<th>Compounds</th>
<th>400K</th>
<th>600K</th>
<th>800K</th>
<th>1000K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ce}_2\text{(WO}_4\text{)}_3$</td>
<td>2</td>
<td>7</td>
<td>$1.58\times10^3$</td>
<td>$3.16\times10^5$</td>
</tr>
<tr>
<td>$\text{TbWO}_4$</td>
<td>6</td>
<td>17</td>
<td>$6.31\times10^2$</td>
<td>$3.31\times10^5$</td>
</tr>
<tr>
<td>$\text{Dy}_2\text{(WO}_4\text{)}_3$</td>
<td>10</td>
<td>18</td>
<td>$2.82\times10^2$</td>
<td>$1.58\times10^4$</td>
</tr>
<tr>
<td>$\text{Ho}_2\text{(WO}_4\text{)}_3$</td>
<td>2</td>
<td>3</td>
<td>$1.00\times10^2$</td>
<td>$3.98\times10^4$</td>
</tr>
<tr>
<td>$\text{Er}_2\text{(WO}_4\text{)}_3$</td>
<td>2</td>
<td>3</td>
<td>$2.51\times10^1$</td>
<td>$2.82\times10^4$</td>
</tr>
<tr>
<td>$\text{Yb}_2\text{(WO}_4\text{)}_3$</td>
<td>2</td>
<td>11</td>
<td>$3.98\times10^2$</td>
<td>$6.31\times10^4$</td>
</tr>
</tbody>
</table>
(v) Interfacial polarization due to air gap between electrodes and material surface.

There is no chance for the existence of thermally generated charge carriers at lower side of temperature ($T < 500K$). The lower value of $K'$ below 500K indicates that free charge carriers generated from impurities is also small. The slow increase of $K'$ for all indicates that the number of thermally generated charge carries below 500K are small. This rules out the possibility of strong space charge polarizability. Well made electrode rules out the chance of interfacial polarization. Therefore this slow increase seems to be the combined effect of lattice and electronic polarizabilities of individual ions. The increase of these polarizabilities seems to compensate the slight decrease of polarizability due to decrease in the number of ions per unit volume following the lattice expansion with temperature. However, it must be noticed that the increase of $K'$ with $T$ is very slow in comparison to the variation one expects for ionic solid or even for the oxides of light rare earth elements (Lal 1980). This indicates that either thermal expansion of these materials is very small or they have some other kind of polarization mechanism.

It is seen from Figs. 6.1 to 6.6 that the rate of increase of dielectric constant becomes extremely faster at high temperature ($T>T_1$). This is attributed due to the space charge polarization of thermally generated charge carriers (small polarons). They are formed as a result of the interaction of thermally generated electrons or holes with the longitudinal optical mode frequency of the lattice. Swell (1963) pointed out that the polarons can significantly increase the value of dielectric
FIG: 6.1  
(a) PLOTS OF LOGARITHM OF DIELECTRIC CONSTANT (Log $K'$) AGAINST ABSOLUTE TEMPERATURE (T)  
(b) PLOTS OF LOGARITHM OF DIELECTRIC LOSS (Log $K''$) AGAINST ABSOLUTE TEMPERATURE (T)  
(c) PLOTS OF QUALITY FACTOR ($Q$) VS ABSOLUTE TEMPERATURE (T)
FIG: 6.2  
(a) PLOTS OF LOGARITHM OF DIELECTRIC CONSTANT (Log K') AGAINST ABSOLUTE TEMPERATURE (T)  
(b) PLOTS OF LOGARITHM OF DIELECTRIC LOSS (Log K') AGAINST ABSOLUTE TEMPERATURE (T)  
(c) PLOTS OF QUALITY FACTOR (Q) VS ABSOLUTE TEMPERATURE (T)
FIG: 6.3  (a) PLOTS OF LOGARITHM OF DIELECTRIC CONSTANT (Log K') AGAINST ABSOLUTE TEMPERATURE (T)
(b) PLOTS OF LOGARITHM OF DIELECTRIC LOSS (Log K') AGAINST ABSOLUTE TEMPERATURE (T)
(c) PLOTS OF QUALITY FACTOR (Q) VS ABSOLUTE TEMPERATURE (T)
FIG. 4
(a) PLOTS OF LOGARITHM OF DIELECTRIC CONSTANT (Log $K'$) AGAINST ABSOLUTE TEMPERATURE (T)
(b) PLOTS OF LOGARITHM OF DIELECTRIC LOSS (Log $K''$) AGAINST ABSOLUTE TEMPERATURE (T)
(c) PLOTS OF QUALITY FACTOR (Q) VS. ABSOLUTE TEMPERATURE (T)
Figure 5: (a) Plots of logarithm of dielectric constant ($\log K'$) against absolute temperature ($T$).
(b) Plots of logarithm of dielectric loss ($\log K''$) against absolute temperature ($T$).
(c) Plots of quality factor ($Q$) vs absolute temperature ($T$).
(a) $Yb_2(WO_4)_3$

(b) 775K

(c) 775K

FIG. 6.6 (a) PLOTS OF LOGARITHM OF DIELECTRIC CONSTANT ($\log K'$) AGAINST ABSOLUTE TEMPERATURE ($T$)
(b) PLOTS OF LOGARITHM OF DIELECTRIC LOSS ($\log K'$) AGAINST ABSOLUTE TEMPERATURE ($T$)
(c) PLOTS OF QUALITY FACTOR ($Q$) VS ABSOLUTE TEMPERATURE ($T$)
constant. Polarizability will be proportional to the number of charge carriers, which is exponentially increasing with temperature. The dielectric loss also show a faster increase above certain critical temperature. Table 6.4 shows that the observed break temperature \( T_{K^{'}} \) in \( K^{'\prime} \) and temperature \( T_1 \) at which phase transition is observed in \( \log \sigma \) vs \( T^{-1} \) plot. Both the temperature are nearly same except in \( Yb_2(WO_4)_3 \). Thus it appears that thermally generated charge carriers play a significant role at higher temperature.

**TABLE-6.4**

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Ce(_2)(WO(_4))(_3)</th>
<th>TbWO(_4)</th>
<th>Dy(_2)(WO(_4))(_3)</th>
<th>Ho(_2)(WO(_4))(_3)</th>
<th>Er(_2)(WO(_4))(_3)</th>
<th>Yb(_2)(WO(_4))(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_{K^{'}} )</td>
<td>583</td>
<td>700</td>
<td>600</td>
<td>763</td>
<td>795</td>
<td>775</td>
</tr>
<tr>
<td>( T_1 )</td>
<td>583</td>
<td>699</td>
<td>588</td>
<td>763</td>
<td>794</td>
<td>505</td>
</tr>
</tbody>
</table>

**6.4 CONCLUSION**

1. The studied tungstate compounds have relatively high value of dielectric constant and low value of dielectric loss around 400K.
2. The dielectric constant and loss have very slow increase up to temperature. However above this increase becomes more faster.
   
   The value of is different for different compounds.
3. The highest value of \( K^{'\prime} (=159) \) occurs for TbWO\(_4\) and lowest value
(K´=25) for Er₂(WO₄)₃ and Yb₂(WO₄)₃.

4. The reason for faster increase of K´ and K´´ at higher temperature is due to space charge effect of thermally generated charge carriers.
CHAPTER-VII

MAGNETIC SUSCEPTIBILITY OF TUNGSTATE COMPOUNDS AT HIGH TEMPERATURE

7.1 INTRODUCTION


7.2 MATERIALS AND EXPERIMENTAL PROCEDURES

All the studied tungstate compounds were prepared by firing stoichiometric mixture of tungston and rare-earth oxides in compressed form of air around 1400K for 50 hrs, with one intermediate grinding.
The XRD analysis shows that this procedure results in single phase compound and no part of the starting materials remains unreacted. The details are given in chapter IV. Magnetic susceptibility measurement was done on powdered samples using Faraday’s method. The details about the measurement are given in chapter III.

7.3 RESULTS AND DISCUSSION

The magnetic susceptibility measurement of all studied compounds were done in heating and cooling cycles. No hysteresis was observed and \( \chi_M \) values were found to be same in heating and cooling cycles, although a small loss of weight is detected for all the compounds in heating cycle. The results were given in Figs. 7.1 to 7.6 for \( \text{Ce}_2(\text{WO}_4)_3 \), \( \text{TbWO}_4 \), \( \text{Dy}_2(\text{WO}_4)_3 \), \( \text{Ho}_2(\text{WO}_4)_3 \), \( \text{Er}_2(\text{WO}_4)_3 \) and \( \text{Yb}_2(\text{WO}_4)_3 \) respectively. In all these figures molar magnetic susceptibility \( (\chi_M) \) and its inverse \( (\chi_M^{-1}) \) have been plotted as a function of absolute temperautre.

It is seen from the figures that \( \chi_M^{-1} \) vs T plots are linear and can be expressed by the relation

\[
\chi_M^{-1} = \frac{T - \theta_p}{C_M}
\]

Where \( \theta_p \) is paramagnetic Curie temperature and \( C_M \) is the molar Curie constant.

All the studied compounds are magnetically simple because they contain only one type of magnetic ion i.e. trivalent rare-earth ions. The magnetic interaction exists in these compounds is \( \text{R}^{3+} - \text{R}^{3+} \) (R = Rare-earth). Thus at temperature much higher than ordering temperature, the molar magnetic susceptibility of all these compounds can be approximated by the realtion
Where \( N \) is Avogadro number, and \( \mu \) magneton numbers of magnetic ion \( \text{R}^{3+} \) ions, \( \theta_p \) is the paramagnetic Curie temperatures. Eq. 7.2 can also be written as

\[
\chi_M^{-1} = \frac{T - \theta_p}{C_M}
\]  

(7.2)

Comparing Eq. (7.1) and (7.3), we have

\[
\chi_M^{-1} = \frac{3k(T - \theta_p)}{N\mu_0\mu_\beta^2\bar{P}^2}
\]  

(7.3)

This yields

\[
\bar{P} = \left[ \frac{3k}{N\mu_0\mu_\beta^2} \right]^{1/2}
\]  

(7.5)

Thus experimental value of \( \bar{P} \) can be evaluated from the value of \( \chi_M^{-1} \) obtained from \( \chi_M^{-1} \) vs T plot. The theoretical values \( \bar{P} \) of has been already known. The different constants (Morrish 1965 and Goodenough 1965) have been evaluated using the straight part of the curve (Fig. 7.1 to 7.6). The theoretical and experimental values of \( \bar{P} \) with magnetic ions are given in Table 7.1 and the values of \( \theta_p \) and \( C_M \) are given in Table 7.2.

There is a good agreement between the theoretical and experimental values of (Van Vleck 1932), which shows that ionic moments involved in the magnetization process concern the tri-positive rare-earth ions. This good agreement between theoretical and experimental values of together with no deviation of the \( \chi_M^{-1} \) vs T curves show a straight line even at high
temperature also suggests that the 4f magnetic electrons are completely localised at the ions. Thus any question of their participation in the electrical conduction does not arise. This means that some other electrons are responsible for the semiconducting properties of these compounds.

FIG. 7.1 (a) VARIATION OF MOLAR MAGNETIC SUSCEPTIBILITY ($\chi_M$) WITH ABSOLUTE TEMPERATURE OF Ce$_2$(WO$_4$)$_3$
(b) VARIATION OF INVERSE OF MOLAR MAGNETIC SUSCEPTIBILITY ($\chi_M^{-1}$) WITH ABSOLUTE TEMPERATURE OF Ce$_2$(WO$_4$)$_3$
FIG. 7.2 (a) VARIATION OF MOLAR MAGNETIC SUSCEPTIBILITY ($\chi_M$) WITH ABSOLUTE TEMPERATURE OF TbWO$_4$
(b) VARIATION OF INVERSE OF MOLAR MAGNETIC SUSCEPTIBILITY ($\chi_M^{-1}$) WITH ABSOLUTE TEMPERATURE OF TbWO$_4$
FIG. 7.3 (a) VARIATION OF MOLAR MAGNETIC SUSCEPTIBILITY ($\chi_M$) WITH ABSOLUTE TEMPERATURE OF Dy$_2$(WO$_4$)$_3$

(b) VARIATION OF INVERSE OF MOLAR MAGNETIC SUSCEPTIBILITY ($\chi_M^{-1}$) WITH ABSOLUTE TEMPERATURE OF Dy$_2$(WO$_4$)$_3$
FIG. 7.4 (a) VARIATION OF MOLAR MAGNETIC SUSCEPTIBILITY ($\chi_M$) WITH ABSOLUTE TEMPERATURE OF $\text{HO}_2(\text{WO}_4)_3$

(b) VARIATION OF INVERSE OF MOLAR MAGNETIC SUSCEPTIBILITY ($\chi_M^{-1}$) WITH ABSOLUTE TEMPERATURE OF $\text{HO}_2(\text{WO}_4)_3$
FIG 7.5 (a) VARIATION OF MOLAR MAGNETIC SUSCEPTIBILITY ($\chi_M$) WITH ABSOLUTE TEMPERATURE OF $\text{Er}_2(\text{WO}_4)_3$

(b) VARIATION OF INVERSE OF MOLAR MAGNETIC SUSCEPTIBILITY ($\chi_M^{-1}$) WITH ABSOLUTE TEMPERATURE OF $\text{Er}_2(\text{WO}_4)_3$
FIG. 7.6 (a) VARIATION OF MOLAR MAGNETIC SUSCEPTIBILITY ($\chi_M$) WITH ABSOLUTE TEMPERATURE OF Yb$_2$(WO$_4$)$_3$

(b) VARIATION OF INVERSE OF MOLAR MAGNETIC SUSCEPTIBILITY ($\chi_M^{-1}$) WITH ABSOLUTE TEMPERATURE OF Yb$_2$(WO$_4$)$_3$
### TABLE-7.1

PARAMAGNETIC CURIE TEMPERATURE ($\theta_p$) AND MOLAR CURIE CONSTANT OF THE STUDIED COMPOUNDS

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\theta_p$ (K)</th>
<th>$\times 10^5$ (m³Kmole⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ce}_2(\text{WO}_4)_3$</td>
<td>- 69</td>
<td>0.980</td>
</tr>
<tr>
<td>$\text{TbWO}_4$</td>
<td>- 197</td>
<td>14.272</td>
</tr>
<tr>
<td>$\text{Dy}_2(\text{WO}_4)_3$</td>
<td>- 12</td>
<td>17.542</td>
</tr>
<tr>
<td>$\text{Ho}_2(\text{WO}_4)_3$</td>
<td>- 31</td>
<td>17.444</td>
</tr>
<tr>
<td>$\text{Er}_2(\text{WO}_4)_3$</td>
<td>- 13</td>
<td>14.112</td>
</tr>
<tr>
<td>$\text{Yb}_2(\text{WO}_4)_3$</td>
<td>- 43</td>
<td>3.124</td>
</tr>
</tbody>
</table>

### TABLE-7.2

THEORETICAL AND EXPERIMENTAL VALUES OF AVERAGE MAGNETON NUMBER PER MAGNETIC ION OF THE STUDIED COMPOUNDS

<table>
<thead>
<tr>
<th>Compound</th>
<th>Magnetic ion</th>
<th>Theoretical Values</th>
<th>Experimental Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ce}_2(\text{WO}_4)_3$</td>
<td>$\text{Ce}^{3+}$</td>
<td>2.54</td>
<td>2.50</td>
</tr>
<tr>
<td>$\text{TbWO}_4$</td>
<td>$\text{Tb}^{3+}$</td>
<td>9.72</td>
<td>9.56</td>
</tr>
<tr>
<td>$\text{Dy}_2(\text{WO}_4)_3$</td>
<td>$\text{Dy}^{3+}$</td>
<td>10.65</td>
<td>10.59</td>
</tr>
<tr>
<td>$\text{Ho}_2(\text{WO}_4)_3$</td>
<td>$\text{Ho}^{3+}$</td>
<td>10.61</td>
<td>10.56</td>
</tr>
<tr>
<td>$\text{Er}_2(\text{WO}_4)_3$</td>
<td>$\text{Er}^{3+}$</td>
<td>9.58</td>
<td>9.50</td>
</tr>
<tr>
<td>$\text{Yb}_2(\text{WO}_4)_3$</td>
<td>$\text{Yb}^{3+}$</td>
<td>4.54</td>
<td>4.46</td>
</tr>
</tbody>
</table>
The values of $\theta_p$ are negative for studied compounds suggesting a possible antiferromagnetic ordering of these compounds at lower temperatures. However, such small values of $\theta_p$ can also be due purely to the crystal field effect (Thomas and Seinko 1974) with a little contribution from simple dipole-dipole interaction between the magnetic ions.

It is difficult to say anything about the type of exchange interaction in these compounds which leads to antiferromagnetic ordering. A better understanding of the Re$^{3+}$–O–W–O–Re$^{3+}$ interaction needs a low temperature study of magnetic susceptibility, remanance magnetisation and neutron diffraction. Unfortunately we do not have the facilities for such studies in our laboratory.

7.4 CONCLUSION

On the basis of high temperature magnetic susceptibility studies and its analysis following conclusion can be drawn:

1. In the studied compounds the magnetic ions contribute towards magnetic susceptibility as per their effective magneton number.
2. All the studied compounds exhibit typical Curie-Weiss law behavior at higher temperature. They have negative values of paramagnetic Curie temperature indicating antiferromagnetic ordering at lower temperature.

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