



Electrical Transport Properties of $Ce_2(WO_4)_3$, $Dy_2(WO_4)_3$ and $Ho_2(WO_4)_3$

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The tungstate compounds of the type $R_2(WO_4)_3$ (where R = Ce, Dy and Ho) have been prepared by a solid state reaction technique and characterized by XRD, DTA, TG and DTG. The XRD characterization suggests the formation of single phase orthorhombic structure at room temperature. The electrical conductivity (σ) measurements on the pressed pellets have been reported in the temperature range 303 to 1103 K. It has been found that these compounds are essentially electronic conductors with σ values lying in the order of $10^{-6} \Omega^{-1} m^{-1}$ around 300 K and increases with increase of temperature.

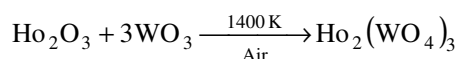
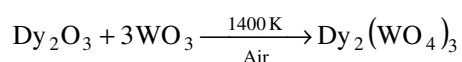
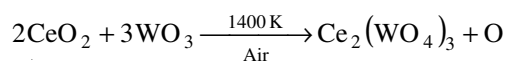
Key Words: Electrical conductivity, XRD, DTA, TG, DTG, $R_2(WO_4)_3$ (where R = Ce, Dy and Ho).

INTRODUCTION

Mixed rare-earth and transition metal oxides have been the subject of study due to their interesting magnetic, dielectric, electrical transport properties and their applications¹. Several such compounds have been investigated in the past^{2,3}. Some of these studies have been reported earlier^{4,5}. A quantitative understanding and semiquantitative analysis of the conduction mechanism can be presented by studying the electrical conductivity as a function of various parameters⁶⁻⁸. This paper reports XRD, DTA, TG, DTG and electrical transport mechanism of $Ce_2(WO_4)_3$, $Dy_2(WO_4)_3$ and $Ho_2(WO_4)_3$.

EXPERIMENTAL

Sample preparation: The starting materials CeO_2 , Dy_2O_3 and Ho_2O_3 of purity 99.9 % and WO_3 of purity 99.8 % (procured from Alfa Aesar, A Johnson Matthey Company, USA). The stoichiometric amounts of these oxides were mixed and heated in a silica crucible for 50 h at a temperature of 1400 K followed by one intermediate grinding and the final product was cooled down slowly. The prepared compounds undergo the following solid state reactions.



The weight loss corresponding to oxygen at right hand side of the reaction was observed in $Ce_2(WO_4)_3$.

To get confirmation regarding the complete formation of the compounds, X-ray diffraction pattern of the sample was taken at room temperature using $CuK\alpha$ line ($\lambda = 0.15418$ nm). The DTA, TG and DTG studies of the compounds of the powders of $Ce_2(WO_4)_3$, $Dy_2(WO_4)_3$ and $Ho_2(WO_4)_3$ were carried out in nitrogen using a thermal analyser (Perkin-Elmer Pyris) at a heating rate of 10 °C/min and flow rate of 100 mL/min from 50 to 850 °C.

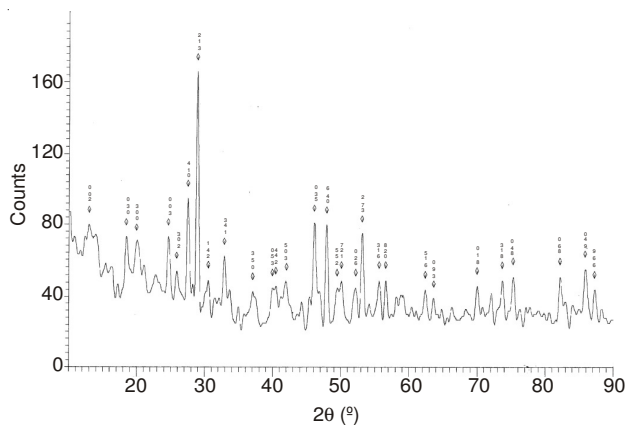
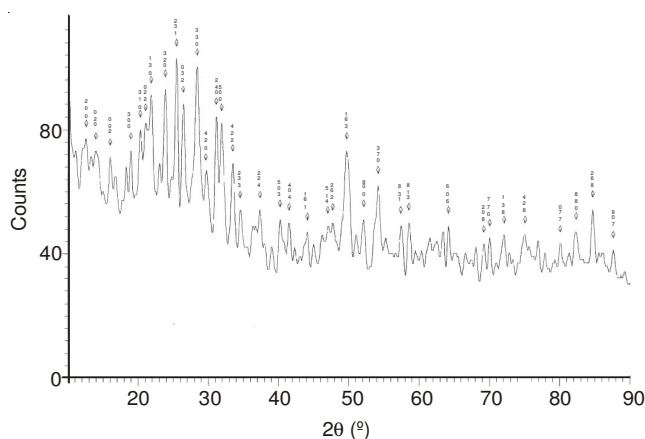
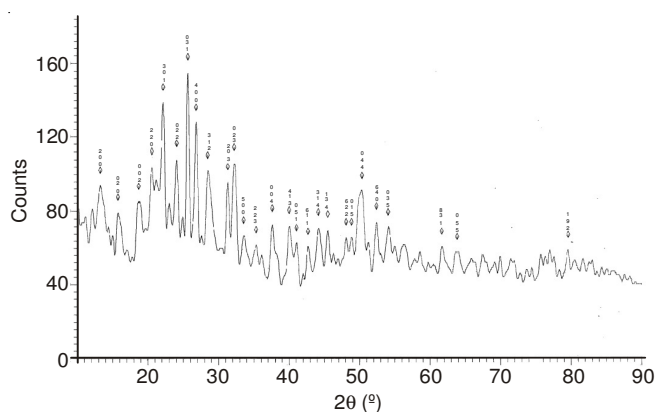
The measurement of electrical conductivity of few pellets of tungstate compounds have been carried out in air in temperature range 303 to 1103 K. The measurements have been done on pellets made at $P > 6.8 \times 10^8$ Nm⁻² and sintered at 1200 K for 50 h.

RESULTS AND DISCUSSION

The room temperature XRD pattern of $Ce_2(WO_4)_3$, $Dy_2(WO_4)_3$ and $Ho_2(WO_4)_3$ are shown in Figs. 1-3. The d_{hkl} values have been calculated by using relation:

$$d_{hkl} = \frac{\lambda}{2 \sin \theta} \quad (1)$$

Using above relation d_{hkl} values are calculated from the XRD pattern and structures of the compounds were resolved. All the peaks have been assigned with proper hkl values. All the compounds are in single phase and are found orthorhombic unit cell with cells parameters a_0 , b_0 and c_0 as given in Table-1.

Fig. 1. Room Temperature XRD of $\text{Ce}_2(\text{WO}_4)_3$ Fig. 2. Room Temperature XRD of $\text{Dy}_2(\text{WO}_4)_3$ Fig. 3. Room Temperature XRD of $\text{Ho}_2(\text{WO}_4)_3$

Compounds	Lattice parameters		
	a_0 (nm)	b_0 (nm)	c_0 (nm)
$\text{Ce}_2(\text{WO}_4)_3$	1.33500	1.44240	1.07820
$\text{Dy}_2(\text{WO}_4)_3$	1.40504	2.26964	1.10782
$\text{Ho}_2(\text{WO}_4)_3$	1.33638	1.12530	0.94900

The DTA, TG and DTG trace of compounds are shown in Figs. 4-6. DTA curves of each compound show an endothermic peak except $\text{Ce}_2(\text{WO}_4)_3$. The peak temperature are given in Table-2.

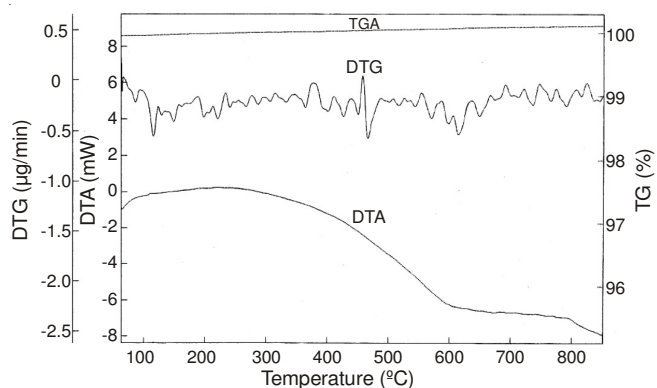
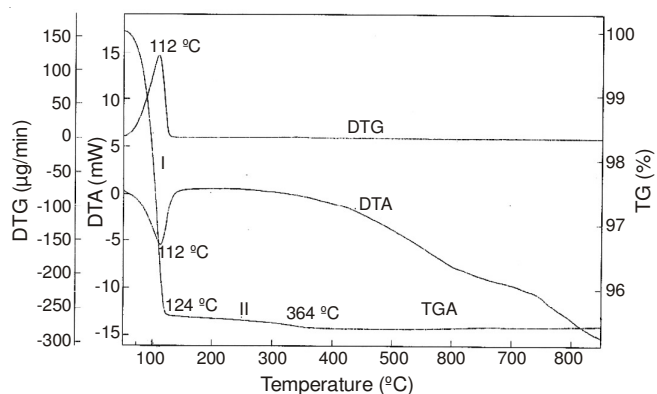
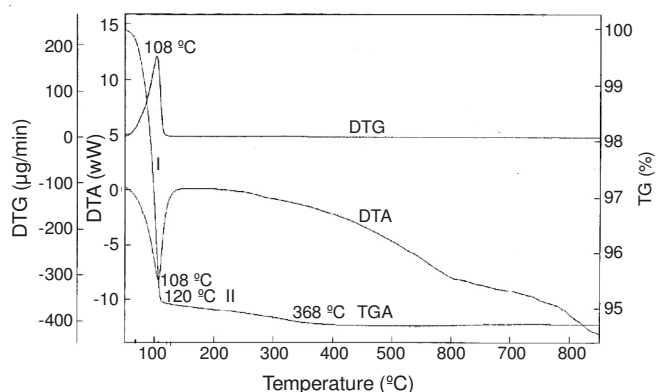
Fig. 4. DTA, TG and DTG curve of $\text{Ce}_2(\text{WO}_4)_3$ Fig. 5. DTA, TG and DTG curve of $\text{Dy}_2(\text{WO}_4)_3$ Fig. 6. DTA, TG and DTG curve of $\text{Ho}_2(\text{WO}_4)_3$

TABLE-2
ENDOTHERMIC PEAK TEMPERATURES IN DTA AND
THE WEIGHT LOSS % CALCULATED FROM TGA
CURVES FOR ALL THE COMPOUNDS

Compd.	Endothermic peak temp. (°C)	Weight loss % in the			
		1 st step		2 nd step	
		Temp. region (°C)	Weight loss (%)	Temp. region (°C)	Weight loss (%)
$\text{Dy}_2(\text{WO}_4)_3$	112	50-124	4.6	124-364	0.13
$\text{Ho}_2(\text{WO}_4)_3$	108	50-120	4.9	120-368	0.30

In TG curves, the sample losses mass in two successive steps I and II except $\text{Ce}_2(\text{WO}_4)_3$ in which mass loss is zero. The weight loss (%) and temperature region is shown in Table-2 for each compound.

Such a small loss in mass is due to moisture. No further mass loss appear over higher temperature in each compounds which indicates that the compounds are stable and do not show decomposition upto 850 °C.

DTG curves of each compounds show a peak except $\text{Ce}_2(\text{WO}_4)_3$. In compounds $\text{Dy}_2(\text{WO}_4)_3$ and $\text{Ho}_2(\text{WO}_4)_3$ the temperature on the DTG curves at which the rate of mass change is maximum are 112 and 108 °C respectively.

The measurement of electrical conductivity of all the studied compounds were done on pressed pellets in heating and cooling cycles. The variation of $\log \sigma$ with inverse of absolute temperature (T^{-1}) for all compounds are shown in Fig. 7. It is seen from this figure that σ values for these compounds are between 10^{-6} to $10^{-3} \Omega^{-1} \text{m}^{-1}$ in the temperature range 303-1103 K. Each plot can be divided into two linear ranges except $\text{Ce}_2(\text{WO}_4)_3$ which have three ranges namely range I lying between $T < T_1$, range II $T_1 < T < T_2$ and range III for $T > T_2$. The temperature T_1 and T_2 are termed as phase transition or break temperature.

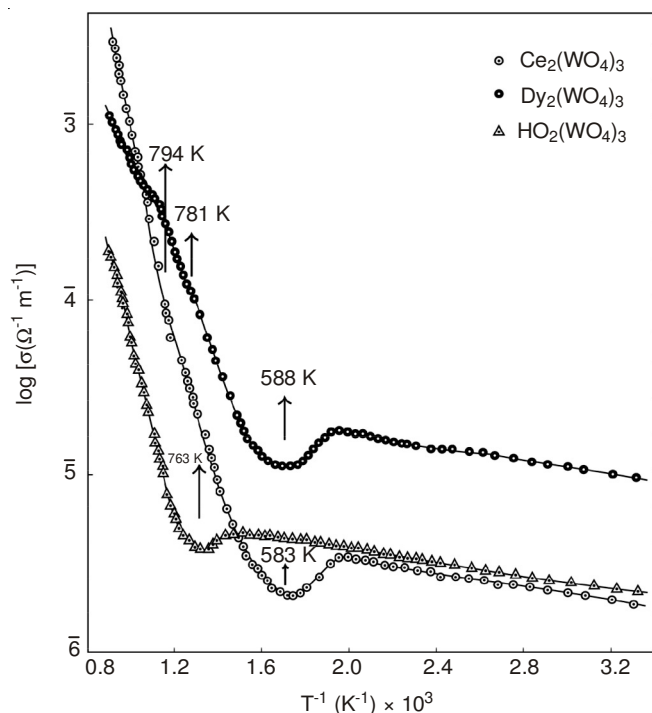


Fig. 7. Plots of logarithm of electrical conductivity ($\log \sigma$) against inverse of absolute temperature (T^{-1})

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

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

The values of pre-exponential constant σ_0 and activation energy (E_a) have been evaluated from the experimental plot and are given in Table-3 together with the values of T_1 and T_2 .

Around 300 K 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 $\text{Dy}_2(\text{WO}_4)_3$ and lowest for $\text{Ce}_2(\text{WO}_4)_3$. The slope of $\log \sigma$ vs. T^{-1} plots for the first temperature range is small (*ca.* 0.1 eV) for all the studied compounds. The pre-exponential constant (σ_0) for all the studied compounds in this temperature range are also small (*ca.* 10^{-5} to $10^{-4} \text{W}^{-1} \text{m}^{-1}$). 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 583 K for $\text{Ce}_2(\text{WO}_4)_3$, 588 K for $\text{Dy}_2(\text{WO}_4)_3$ and 763 K for $\text{Ho}_2(\text{WO}_4)_3$. This probably reflects phase transition temperature of the solid⁹.

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

$$\sigma = \sigma_0 \exp\left(\frac{-E_g}{2kT}\right) \quad (3)$$

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

$$\sigma = \sigma_0 \exp\left\{-\left(\frac{\theta}{T}\right) - \left(\frac{E_g}{2kT}\right)\right\} \quad (4)$$

where θ is the Debye temperature and E_g is the band gap of the solid, which is the expression of the σ 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:

$$\sigma = AT^{1/2} \exp\left(\frac{-E_a}{kT}\right) \quad (5)$$

TABLE-3
VALUES OF PRE-EXponential CONSTANT (σ_0) AND E_a TOGETHER WITH T_1 AND T_2 IN DIFFERENT REGION OF $\log \sigma$ vs. T^{-1} PLOT OF THE STUDIED COMPOUNDS

Compounds	$T < T_1$			$T_1 < T < T_2$			$T > T_2$	
	σ_0 ($\Omega^{-1} \text{m}^{-1}$)	E_a (eV)	T_1 (K)	σ_0 ($\Omega^{-1} \text{m}^{-1}$)	E_a (eV)	T_1 (K)	σ_0 ($\Omega^{-1} \text{m}^{-1}$)	E_a (eV)
$\text{Ce}_2(\text{WO}_4)_3$	4.75×10^{-5}	0.09	583	3.75×10^9	2.02	794	1.87×10^{13}	3.25
$\text{Dy}_2(\text{WO}_4)_3$	2.94×10^{-4}	0.10	588	8.88×10^7	1.76	—	—	—
$\text{Ho}_2(\text{WO}_4)_3$	6.37×10^{-5}	0.10	763	1.12×10^9	2.57	—	—	—

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 polarisable suggests that the charge carriers will be polarons as discussed by so many authors¹⁰⁻¹⁵ in $3d$ and $4f$ compounds. In any case polaron is more general and may include electron or hole type of conduction in extreme limit of very weak coupling.

Conclusion

XRD studies confirm that the studied compounds have single phase orthorhombic structure at room temperature. DTA, TG and DTG studies show that the compounds are stable above certain temperature. The electrical conductivity measurement shows that these compounds are semiconducting materials with a electrical conductivity value of the order of $10^{-6} \Omega^{-1} \text{m}^{-1}$ around 300 K which becomes of the order of $10^{-4} \Omega^{-1} \text{m}^{-1}$ to $10^{-3} \Omega^{-1} \text{m}^{-1}$ around 1103 K. 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 $\text{Ce}_2(\text{WO}_4)_3$. The maximum conductivity is observed for $\text{Dy}_2(\text{WO}_4)_3$ and lowest for $\text{Ce}_2(\text{WO}_4)_3$.

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