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Electrical Transport Studies of Rare- Earth Titanates

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ABSTRACT -

This research paper reports the measurement of electrical conductivity (σ) and seeback coefficient (S).At high temperature the electrical conductivity (σ) and seeback coefficient (S) gives an idea about conduction mechanism. These compounds have been prepared by solid state reaction technique and characterized by XRD pattern. These are typical semiconductor materials with electrical conductivity value lying in the range $10^{-6}\ \Omega^{-1}\ m^{-1}$ & $10^{-5}\ \Omega^{-1}\ m^{-1}$ around 400K which becomes of the order of $10^{5}\Omega^{-1}\ m^{-1}$to $10^{-6}\ \Omega^{-1}\ m^{-1}$ around 1200. The seeback coefficient (S) becomes large and nearly constant with temperature. The constancy and large value of the seeback coefficient indicates that conduction mechanism is hoping type.

INTRODUCTION:

The material $RTiO_3$ (where R stands for La, Ce, Pr and Sm) have attracted attention due to the surprising verity of physical properties [1-3]. we have already reported the dielectric properties and magnetic behavior of $RTiO_3$ [4, 5]. This paper reports result of our study on the electrical transport studies of $RTiO_3$, no study of this kind has been reported on these compounds. Only $RTiO_3$ have been reported at low temperature [6,7]. The study of seeback coefficient gives the idea about the nature and the number of charge carriers. Thus study of both electrical conductivity and seeback coefficient yield some important information about conduction process in any solid. Using this mythology we have investigated electrical transport mechanism of light rare earth titanates.

EXPERIMENTAL:

PREPARATION AND CHARACTERIZATION OF MATERIALS:

The series of compounds with general formula $RTiO_3$ has been prepared with their common oxides La_2O_3, CeO_2 Pr_6O_{11}, Sm_2O_3 and TiO_2. These materials were produced from standard forms and have stated purity of 99.9%. The stiochiometric amount of these oxides were mixed with TiO_3 and heated in a silica crucible for 50 hrs at a temperature of about 1400K. In this process, the mixture was subjected to one intermediate grinding and the final product was cooled down at a slow rate.

To confirm the complete formation of the prepared compounds, XRD pattern was obtained for each material using CuKα radiation with λ= 0.15418 nm. From XRD pattern the value of interplaner spacing d_{hkl} have been obtained using relation.

$$d_{hkl} = \frac{0.15418}{2\sin\theta}(nm) \qquad (1)$$

From d_{hkl} values, structures of the prepared compounds have been resolved using standard procedure [8].

Measurement of electrical conductivity and seeback coefficients:

The electrical conductivity (σ) measurement of pellets of rare – earth titanates have been carried out in air in temperature range 400K to 1200K. The measurements have been done on pellets made at P>6.28 x $10^8 Nm^{-2}$ and sintered at 1000K for 48 hrs. The variations of log σ with inverse of absolute temperature (T) for different compounds are presented in fig. 1-4.

The seeback coefficient (S) of the pressed pellets has been measured in the temperature range (370 – 1250)K. The result of the measurement carried out on titanates has been presented in fig. 1-4. as S Vs T^{-1} plot.

RESULTS AND DISCUSSION:

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 has been observed in conductivity values during heating and cooling cycles. It is seen from fig. 1-4 that log σ vs T^{-1} plots are linear in specific regions with different slopes. In general they can be divided in three linear regions namely,

(1) $T<T_1$ (2) $T_1 < T < T_2$ (3) $T > T_2$.

The temperature T_1 and T_2 may be termed as transition or break temperature. In each region, they can be expressed by the relation.

$$\sigma = \sigma_0 \exp(-W / KT) \qquad (3)$$

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Where σ_0 is a constant and W is the energy corresponding to the slope of the straight lines. The values of σ_0 and W are different for different titanates and for different regions of the same titanates. The evaluated values of σ_0, W and T_B (T_1 , T_2) has been listed in table 3.

TABLE – 1

The pre- exponential constant (σ_0), Energy (W) and Break temperature ($T_B = T_1$ and T_2)

for the studied rare – earth titanates

$RTiO_3$ with R =	$T<T_1$			$T_1 < T < T_2$			$T > T_2$	
	σ_0 ($\Omega^{-1}m^{-1}$)	W (ev)	T_1 (K)	σ_0 ($\Omega^{-1}m^{-1}$)	W (ev)	T_2 (K)	σ_0 ($\Omega^{-1}m^{-1}$)	W (ev)
La	$7.55x10^{-6}$	0.02	694	$3.97\ x10^{1}$	0.95	1000	$6.24\ x10^{2}$	1.60
Ce	$9.80\ x10^{-6}$	0.02	694	$9.67\ x10^{1}$	0.92	1000	$3.99\ x10^{5}$	1.65
Pr	$3.97\ x10^{-5}$	0.02	671	$3.12\ x10^{2}$	0.95	1000	$1.15\ x10^{6}$	1.65
Sm	$3.10\ x10^{-6}$	0.02	714	$0.52\ x10^{1}$	0.90	1064	$5.82\ x10^{3}$	1.70

We adopt a sign convention for S in which the sign of seeback coefficient is the sign of potential it hot end compared to cold end. In this convention the sign of charged carrier is opposite to the sign of seeback coefficient. Similar conventions has been used by many workers [9,10]. S Vs T^{-1} plot has three linear regions and the slope in each region is very small. The value of S in each linear region can be expressed by the following relation

$$S = \eta T^{-1} + H \qquad (4)$$

Where η is the slope of S Vs T^{-1} plot and H is constant whose value is equal to the intercept on S axis. The evaluated values of η and H for different temperature regions of the studied four titanates together with the seeback temperature (T_B = T_1 and T_2) have been given in table 1.

TABLE -2

The slope (η) of linear S vs T^{-1} plot and constant (H) together with break temperature (T_1 and T_2) for studied rare – earth titanates $RTiO_3$

$RTiO_3$ with R =	$T<T_1$		$T_1 < T < T_2$			$T > T_2$		
	H (v)	H (mvK^{-1})	T_1 (K)	η (v)	H (mvK^{-1})	T_2 (K)	η (v)	H (mvK^{-1})
La	**-0.03**	**-0.86**	**694**	**-0.02**	**-0.29**	**1000**	**-0.13**	**-0.22**
Ce	**-0.03**	**-0.84**	**694**	**-0.02**	**-0.30**	**980**	**-0.13**	**-0.23**
Pr	**-0.03**	**-0.79**	**670**	**-0.02**	**-0.24**	**990**	**-0.13**	**-0.21**
Sm	**-0.05**	**-0.79**	**714**	**-0.05**	**-0.40**	**1064**	**-0.27**	**-0.10**

The intrinsic band conduction, is the dominant conduction mechanism at higher temperature in these solids. The temperature variation of electrical conductivity should be given by the equation [11]

$$\sigma = \sigma_0 \exp(-Eg / 2KT) \quad (5)$$

Where $\sigma_0 = KT^{3/2}\ a^{3/4}\ (1 + C)\ \mu_h$ (6)

with $K = 2e(2\pi k/h^2)^{3/2}\ m_h^{3/2}$, $a = m_e / m_h$ (7)

and $C = \mu_e / \mu_h$.

According to this relation the plot of log σ vs T^{-1} in band condition will be a straight line with a slope of -Eg / 2K. The experimental log σ vs T^{-1} in third range $T > T_2$ plots are actually straight line as shown in fig. 1 – 4. From the slope of the straight line, the energy band gap (Eg) for studied titanates have been evaluated and listed in table 3.

TABLE – 3

Evaluated values of Electrical transport

$RTiO_3$ with R =	Eg (eV)	**A** (m_e/m_h)	C (μ_e/μ_h)	μh (m^2/Vsec)	μe (m^2/Vsec)
La	**3.20**	**0.041**	**0.850**	**1.54×10^{-4}**	**1.29×10^{-4}**
Ce	**3.30**	**0.035**	**0.854**	**1.09×10^{-1}**	**0.93×10^{-1}**
Pr	**3.30**	**0.048**	**0.854**	**2.47×10^{-1}**	**2.11×10^{-1}**
Sm	**3.40**	**0.018**	**0.889**	**2.14×10^{-3}**	**1.90×10^{-3}**

It is seen from the table that the value of E_g is of the order of 3ev which seems quite reasonable.

The temperature variation of the seeback coefficient (S) for titanates should be the equation [12]

S = Eg(c-1) / 2e (c + 1) T + 2 (c – 1)k / (c + 1) e + (¾) (k/e) ln (m_e / m_n) (8)

In bond conduction, one expects the temperature variation of μ_e and μ_n, and that of m_e and m_n to be similar. It is therefore reasonable to assume that their ratios will be constant in the studied temperature range $T > T_2$. Hence the second and third terms in the above equation will remain with temperature. Thus the above expression can be written as,

$S = \eta / T + H$ for $T > T_2$

where $\eta = Eg /2e) (c-1) /(c + 1)$ (9) and

$H = 2(c-1 /c+1) (k/e)+ (3/4) (k/e) \ln a$ (10)

The S vs T^{-1} plots should be straight line which has been found experimentally true for all studied titanates. From S vs T^{-1} plots, η and H can be evaluated. The value of Eg has already been obtained from log σ vs T^{-1} plots for each solid. Knowing the experimental value of η, and Eg. For each titanates in the third region $T > T_2$, both a and c can be evaluated using expression (9) and (10).

The evaluated values of a and c has been listed in table – 5. From known values of a, c and σ_0, one can evaluate the value of μ_h and μ_e in terms of m_h and m_e using expression (6). The exact value of m_h and m_e is not known for any of these solids however, one can estimate the value of μ_h and μ_e by taking the mass of the majority charge carriers (holes) to be equal to the mass of a free electron. Taking $m_h = m_0$, the computed value of μ_h and μ_e together with the value of a and c have been given in table – 3.

It is clear from table 4 that mobility of the charge carriers (holes) are of the order of 10^{-1} - 10^{-4} (m^2/V-sec). In bond conduction one expects the mobility of charge carriers to be of the order of 10^{-3}(m^2/V-sec) or more.[12] This mechanism dominates above T = 1000K (i.e for region $T > T_2$). However for region $T_1 < T < T_2$ (below T = 1000K), the slope of log σ vs T^{-1} plots for different $RTiO_3$ changes and become less. The thermoelectric power (S) becomes large and nearly constant with temperature. The constancy of (S) indicates the constancy in the number of charge carriers. It appears that impurity conduction has taken up the electrical conduction.

However sign of the charge carrier remains same (i.e holes). The constancy and the large value of the thermoelectric power indicating that conduction mechanism is hoping type [13].

Table- 4

Evaluated values of hopping mobility **(**μ) at different temperature.

$RTiO_3$ with R =	μ ($m^2\ v^{-1}\ s^{-1}$) at tem equals to			
	700K	800K	900K	1000K
La	$3.65X10^{-12}$	$3.20X10^{-11}$	$1.36X10^{-10}$	$4.19X10^{-10}$
Ce	$7.24X10^{-12}$	$3.07X10^{-11}$	$2.00X10^{-10}$	$5.92X10^{-10}$
Pr	$3.61X10^{-12}$	$3.16X10^{-11}$	$1.35X10^{-10}$	$4.15X10^{-10}$
Sm	$1.07X10^{-11}$	$6.57X10^{-11}$	$2.56X10^{-10}$	$7.30X10^{-10}$

It is clear from this table the mobility of charge carriers is appropriate for hoping conduction. It confirms the conduction via hoping mechanism.

CONCLUSION-

These are typical semiconducting materials. The majority charge carriers are holes. Above 1000K the intrinsic band conduction is dominate conduction mechanism. Below 1000K the conduction mechanism is hoping type. These are essentially electronic conductors and have almost no ionic conductivity over the temperature range 400-1200K.

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