THEORETICAL STUDY ON THE ELECTRICAL PROPERTIES OF SOME SEMICONDUCTING RARE EARTH CHALCOGENIDES $Sm_{1-x}Eu_xS$ AND $Sm_{1-x}Yb_xS$ UNDER PRESSURE

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A theoretical study on semiconductor rare earth chalcogenides $Sm_{1-x}Eu_xS$ and $Sm_{1-x}Yb_xS$ has been made for deducing electrical transport properties using only two parameters, namely lattice constant and activation energy. The calculated electrical properties electrical resistivity, carrier mobility, carrier concentration, carrier effective mass and dielectric constant are compared with the available experimental results. They are found to be in good agreement with each other. Then, the limitation of this theoretical study has also been discussed in this paper.

1. INTRODUCTION

Semiconducting materials basically have structures depending on the nature of bonding. They have tetrahedral bonds and therefore form cubic or hexagonal structures [1, 2]. They include not only covalent bonds but also ionic bonds. There are different class of semiconductors. One interesting class of semiconductor is rare earth chalcogenides. The study of rare earth monochalcogenides has received much attention because of their interesting properties and technological applications. They crystallize in the NaCl type structure and are semiconducting if the rare earth ion is in the divalent state and metallic if in trivalent state [3]. The atoms of all rare earth elements except Eu, Sm and Yb exist in trivalent state. The divalent Eu, Sm and Yb are particularly ideal as most of them are semiconducting and ionic [4, 5]. It is notable that the Samarium monochalcogenides are black semiconducting solid and they have shown continuous semiconductor to metallic transition under pressure at about 45 and 60 kbar in SmSe and SmTe respectively and discontinuous transition at 6.5 kbar in SmS [6]. These transitions in Samarium monochalcogenides can be used as a pressure sensor [6]. The generation of electric voltage upon moderate heating to 150 °C in Samarium monosulfide makes it useful in thermoelectric power converters [7]. The new phenomenon of self heating upto 866 K and the emf generation is reported in samarium monosulfide after termination of external heating. This effect finds promising applications of conversion of thermal energy into electricity [8-10]. The rare earth chalcogenide glasses finds applications in telecommunication devices, integrated optical systems, gas sensing and

remote sensing devices [11-13]. Because of these technological importance, the understanding of the physical properties of these rare earth chalcogenides seems to be interesting and also requires more investigation on the effect of substitution of Eu and Yb for Sm in SmS as well as the effect of pressure on these compounds. Even though, considerable information is now available on these physical properties, in many cases the data is limited. So, in this paper a theoretical model is developed for determining electrical properties of rare earth chalcogenide compounds. This theoretical study has been carried out on the systems $Sm_{1-x}Yb_xS$ ($x = 0.25$, 0.5 and 0.7) and $Sm_{1-x}Yb_xS$ ($x = 0.2$ and 0.75) at ambient conditions and under pressure from 0 to 16 kbar and the results are compared with the experimental results.

2. THEORETICAL METHODOLOGY

Before going into detail, some important aspects involved in these compounds are discussed. Generally, compound semiconductor materials can be predicted by a simple rule. When the total number of valence electrons of constituent elements are divided by the number of elements comprising the compound and when this ratio gives four, the compound has a tendency to be semiconducting [1, 2]. It is notable that these particular rare earth chalcogenide semiconductors are found to be in semiconducting state when the rare earth ion is divalent and metallic when it is trivalent [14]. It is reported from the magnetic susceptibility studies that for the compounds containing dipositive metal ions, the third valence electrons are highly localized in 4f levels. This would result in a full 4f shell for the ytterbium ions, half full for the europium ions and nearly half full for the samarium ions [15]. The highly localized f electrons do not contribute to the electrical conductivity [16]. Experimental results show that the compounds of Sm, Yb and Eu have no conduction electrons in ground state. The most likely process which gives carriers for conduction is thermal activation of electrons from the 4f shell to the conduction band [16]. Here, the question of which type of scattering is dominant arises. The answer is in favour of acoustic scattering. In the case of acoustic scattering, the electrical conductivity σ can be calculated by using the formula [17-19].

$$\sigma = neu = 1/\rho \tag{1}$$

where n is the carrier concentration, e is the electronic charge, u is the carrier mobility and ρ is the electrical resistivity.

The carrier concentration n can be calculated [20] from the carrier effective mass m^* and activation energy ΔE by the expression,

$$n = \frac{2\left(2\pi m^* kT\right)^{3/2}}{h^3} \exp\left(-\frac{\Delta E}{2kT}\right) \tag{2}$$

where k is the Boltzmann's constant, h is the Plank's constant and T is the temperature.

The effective mass m^* can be given [21] in terms of lattice parameter and an activation energy ΔE as,

$$\frac{m_0}{m^*} = 1 + \frac{2\lambda^2}{m_0 a^2 \Delta E} \tag{3}$$

where m_0 is the electron rest mass and $\lambda^2 = \hbar^2$.

The chalcogenides of Sm, Eu and Yb are ionic semiconductors [22]. In ionic lattices, thermal motion and diffusion always give rise to vacant sites abandoned by one of the lattice ions or excess ions diffusing between the lattice cells. In this case, the ion is surrounded by electrostatic coulomb field which is weaker than that in a vacuum by a factor ε representing dielectric constant of the lattice [23]. An electron moving in this field is deflected from its initial path more strongly, the closer it approaches the ion, the longer it remains in the field which slows down its motion. So, the electron mobility [24] is determined by using the formula,

$$u = \frac{3\varepsilon^2}{16\pi^2 m^* \left[\ln(1+x) - \dfrac{x}{1+x} \right]} \left(\frac{h}{e} \right)^3 \tag{4}$$

The value of x is calculated by the formula,

$$x = \left(\frac{h}{e} \right)^2 \left(\frac{e}{m^*} \right) \left(\frac{3N}{8\pi} \right)^{1/3}$$

where N represents the impurity concentration which is given by,

$$N = \frac{n^2}{2 \left(\dfrac{2\pi m^* kT}{h^2} \right)^{3/4} \exp\left(-\dfrac{\Delta E}{2kT} \right)} \tag{5}$$

The dielectric constant [20] ε is calculated by using the expression,

$$\varepsilon^2 = \frac{13.53}{\Delta E} \cdot \frac{m^*}{m_0} \tag{6}$$

Thus, the electrical properties at ambient condition and under pressure have been calculated for $Sm_{1-x}Yb_xS$ ($x = 0.25, 0.5$ and 0.7) and $Sm_{1-x}Yb_xS$ ($x = 0.2$ and 0.75) by using only two parameters lattice constant and activation energy and the validity of this theoretical model is tested by comparing with available experimental values.

3. CONCLUSIONS

The theoretical study has been made on ternary rare earth chalcogenide compounds as a function of composition x on $Sm_{1-x}Yb_xS$ ($x = 0.25, 0.5$ and 0.7) and $Sm_{1-x}Yb_xS$ ($x = 0.2$ and 0.75). And, the study has been extended for the same compounds under pressure from ambient to 16 kbar. Table 1 gives the values of lattice constant and activation energy used for the present study [24]. The Table 2 gives the calculated values of the electrical properties such as carrier concentration (n), carrier effective mass (m^*), dielectric constant (ε) and carrier mobility (u) of $Sm_{1-x}Yb_xS$ ($x = 0.25, 0.5$

and 0.7) and $Sm_{1-x}Yb_xS$ ($x = 0.2$ and 0.75) as a function of composition x and under pressure. The electrical resistivity values are compared with the reported experimental results for $Sm_{1-x}Yb_xS$ as a function of x in Fig. 1a and the same as a function of a pressure for $x = 0.25$ for the same compound in Fig. 1b. The Figure 2a shows the comparison of validation of theoretical and experimental electrical resistivity under pressure for $Sm_{1-x}Yb_xS$ ($x = 0.5$) and Fig 2b for $Sm_{1-x}Yb_xS$ ($x = 0.2$ and 0.75). They are found to be in good agreement with each other. The limitation of this study is that it can be applied only to semiconductors and not to metals because of the dependence of the activation energy on the energy gap. Therefore, the present study has been restricted only to the semiconductors and not to metals. However, the theoretical study gives a reasonably good description of electrical properties as a function of composition and pressure, using only two parameters lattice constant and activation energy.

(a)   (b)
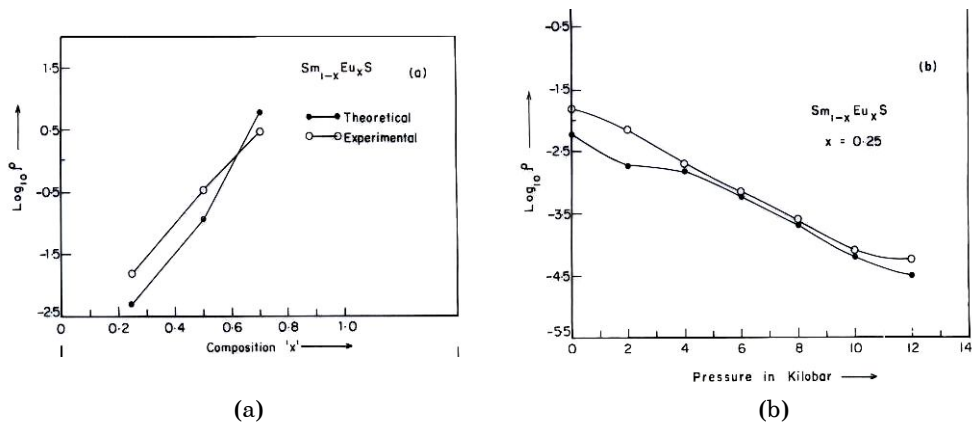
Fig. 1 − *The comparison of electrical resistivity values with the reported experimental values for $Sm_{1-x}Yb_xS$ (a) as a function of x and (b) as a function of pressure for $x = 0.25$*
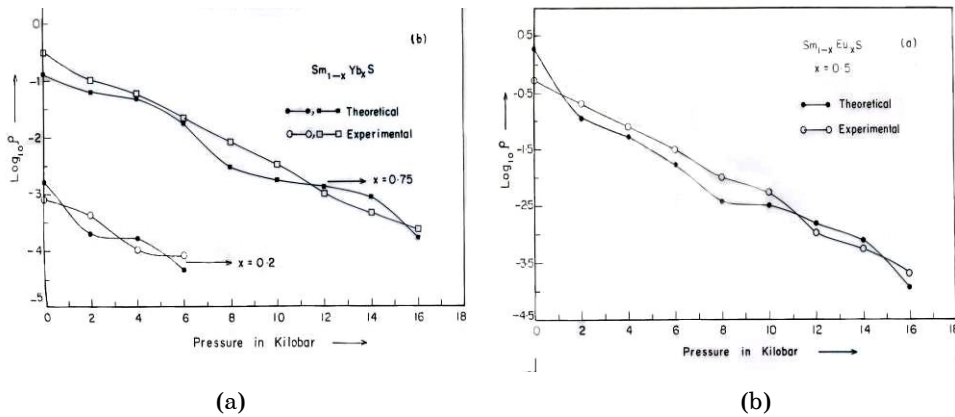

(a)   (b)

Fig. 2 − *The comparison of electrical resistivity values with the reported experimental values as a function of a pressure for (a) $Sm_{1-x}Yb_xS$ ($x = 0.5$) and (b) $Sm_{1-x}Yb_xS$ ($x = 0.2$ and 0.75)*

Table 1 − *The Values of lattice constant (a) and Activation energy (ΔE_g) used for the present study [24]*

Compound	x	P, kbar	a, Å	ΔE_g, eV
$Sm_{1-x}Yb_xS$ ($T = 300$ K)	0.25	-	5.970	0.13
	0.50	-	5.965	0.24
	0.70	-	5.960	0.35
$Sm_{1-x}Yb_xS$ ($T = 300$ K)	0.25	0	5.970	0.180
	0.25	2	5.968	0.156
	0.25	4	5.966	0.132
	0.25	6	5.964	0.108
	0.25	8	5.962	0.084
	0.25	10	5.960	0.060
	0.25	12	5.958	0.036
$Sm_{1-x}Yb_xS$ ($T = 300$ K)	0.5	0	5.970	0.280
	0.5	2	5.969	0.256
	0.5	4	5.967	0.232
	0.5	6	5.967	0.208
	0.5	8	5.966	0.184
	0.5	10	5.964	0.160
	0.5	12	5.962	0.136
	0.5	14	5.960	0.112
	0.5	16	5.956	0.088
$Sm_{1-x}Yb_xS$ ($T = 300$ K)	0.2	0	5.900	0.090
	0.2	2	5.895	0.066
	0.2	4	5.890	0.042
	0.2	6	5.885	0.018
$Sm_{1-x}Yb_xS$ ($T = 300$ K	0.75	0	5.759	0.240
	0.75	2	5.756	0.216
	0.75	4	5.753	0.192
	0.75	6	5.750	0.168
	0.75	8	5.746	0.144
	0.75	10	5.742	0.120
	0.75	12	5.740	0.096
	0.75	14	5.738	0.072
	0.75	16	5.735	0.024

Table 2 − *The Calculated values of the carrier concentration (n), carrier effective mass (m^*), dielectric constant (ε) and carrier Mobility (u)*

Compound	x	P, kbar	n	$m^* \times 10^{-31}$ kg	ε	u, $m^2V^{-1}sec^{-1}$
$Sm_{1-x}Yb_xS$ ($T = 300$ K)	0.25	-	2.286×10^{23}	2.125	4.928	4.949×10^{-4}
	0.50	-	5.208×10^{22}	3.273	4.501	1.006×10^{-4}
	0.70	-	8.683×10^{21}	4.095	4.169	1.208×10^{-4}
$Sm_{1-x}Yb_xS$ ($T = 300$ K)	0.25	0	1.245×10^{23}	2.700	4.721	8.329×10^{-3}
	0.25	2	1.531×10^{23}	2.274	4.653	0.023

	0.25	4	2.236×10^{23}	2.148	4.916	0.019
	0.25	6	2.808×10^{23}	1.835	5.024	0.033
	0.25	8	3.279×10^{23}	1.493	5.139	0.087
	0.25	10	3.381×10^{23}	1.119	5.262	0.308
	0.25	12	2.693×10^{23}	0.705	5.395	0.773
$Sm_{1-x}Yb_xS$ (T = 300 K)	0.5	0	2.779×10^{23}	3.607	4.374	1.668×10^{-4}
	0.5	2	4.068×10^{23}	3.412	4.450	1.304×10^{-4}
	0.5	4	5.887×10^{23}	3.204	4.529	1.928×10^{-4}
	0.5	6	8.403×10^{23}	2.981	4.613	5.714×10^{-4}
	0.5	8	1.178×10^{23}	2.740	4.703	0.016
	0.5	10	1.612×10^{23}	2.478	4.797	0.013
	0.5	12	2.138×10^{23}	2.195	4.896	2.000×10^{-4}
	0.5	14	2.710×10^{23}	1.887	5.003	0.032
	0.5	16	3.209×10^{23}	1.550	5.115	0.162
$Sm_{1-x}Yb_xS$ (T = 300 K)	0.2	0	3.101×10^{23}	1.555	5.065	0.014
	0.2	2	3.314×10^{23}	1.193	5.181	0.096
	0.2	4	2.873×10^{23}	0.796	5.304	0.145
	0.2	6	1.381×10^{23}	0.358	5.437	4.493
$Sm_{1-x}Yb_xS$ (T = 300 K)	0.75	0	4.864×10^{23}	3.127	4.399	9.694×10^{-4}
	0.75	2	6.954×10^{23}	2.912	4.475	1.523×10^{-3}
	0.75	4	9.776×10^{23}	2.682	4.555	1.157×10^{-3}
	0.75	6	1.345×10^{23}	2.435	4.639	2.833×10^{-3}
	0.75	8	1.797×10^{23}	2.168	4.728	1.388×10^{-2}
	0.75	10	2.304×10^{23}	1.879	4.822	1.737×10^{-2}
	0.75	12	1.397×10^{23}	1.567	4.924	4.005×10^{-2}
	0.75	14	3.081×10^{23}	1.227	5.032	2.533×10^{-2}
	0.75	16	2.854×10^{23}	0.856	5.146	0.146

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