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Research Article

THERMOELECTRIC POWER MEASUREMENTS OF ZIRCONIUM SULPHOSELENIDE SINGLE CRYSTALS

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ABSTRACT

Zirconium sulphoselenide single crystals in the form of a series ZrS_xSe_{3-x}. (where $0 \leq x \leq 3$) were grown by chemical vapour transport technique using iodine as a transporting agent. The thermoelectric power of as grown crystals was measured in the temperature range of 303 K to 773 K. The scattering parameter 's', Fermi energy 'E_F', effective density of state 'N_c' and effective mass of electron were carried out for zirconium sulphoselenide single crystals. The negative sign of thermoelectric power depicted their n-type nature within the temperature range studied.

Key Words: *Crystal growth, X-ray Diffraction, Hall Effect, Thermoelectric Effect*

INTRODUCTION

It is well known that the group IV transition metal trichalcogenides have a linear chain structure **(**Furuseth S *et al.,*1975). The linear chain of metal atoms is parallel to the growth axis. Six chalcogen atoms surround each metal atom forming distorted trigonal prisms. The crystals are grown in the form of layers and each chain in the layer is displaced from the neighboring chain by half of the unit cell along the growth-axis. These layers are stacked by weak van der Walls bonds between the chalcogen atoms.

It is essential to possess a detailed knowledge about all the factors of thermoelectric materials, which determines their properties. The major application of the Seebeck effect is about the thermoelectric thermometry that deals with the conversion of thermal energy into electrical energy. As the non-renewable energy sources get dried up quickly, thermoelectric generation is fast and so catching the interest of scientific community as an environment friendly energy source. The generation of electricity at large scale required semiconducting material with significant improvement in their figure of merit. The principle aim of research and development on the thermoelectric materials is to fabricate semiconductors having the figure of merit as high as possible over the temperature range of application of the devices. It is anticipated that the successful development of such materials will lead to new fields of applications for thermoelectric devices and related technologies based on bulk crystals and films.

The thermoelectric power measurements of $ZrSe_3$ single crystals along the chain axis were carried out in the temperature range of 200 K to 400 K (Ikari *et al.,* 1983). It was observed that the thermoelectric power is negative and increases linearly with the reciprocal of temperature. At room temperature, it is 820 μVK^{-1}. Recently a semiconducting material (Zn_4Sb_3) has been developed, which is relatively inexpensive and can be used in more efficient thermoelectric generators for waste heat recovery and automobile industry applications (Caillat *et al.,* 1997).

ZrS_xSe_{3-x} exhibits continuous regions of solid solubility. Diffuse reflectance measurements shows that the $ZrS_{3-x}Se_x$ exhibits semiconducting nature (Brattas and Kjekshus, 1972). These compounds have special interest on account of their structural anisotropy. The need for developing a cheap yet effective method of converting solar energy into electrical or chemical energy stimulated rapid advancement of semiconductor electrochemistry in the past decades. As a result certain useful materials, e.g. metallic chalcogenides that have potential in photovoltaic and photoelectrochemical solar cell studies have attracted attention of crystal growers. Among them, disulphide and diselenide of zirconium present some interesting switching and memory effects (Lee *et al.,* 1969) with some possible application in solid-state solar cell (Tributsch H, 1981).

Optical and electrical properties of the ZrS_3 and $ZrSe_3$ were studied (Patel Kaushik et al. 2005, 2005). The pressure dependence electrical resistance and band gap of zirconium sulphoselenide single crystals were observed. The band gap and electrical resistance decreased with increasing pressure for $ZrSe_3$, $ZrS_{0.5}Se_{2.5}$, $ZrSSe_2$, $ZrS_{1.5}Se_{1.5}$, ZrS_2Se_2, $ZrS_{2.5}Se_{0.5}$ crystals but in ZrS_3 it was inverse because of detachment of sulphur atoms (Patel *et al.,* 2009). The electrical resistivity parallel to c-axis and perpendicular to c-axis were measured with the temperature range 303 K - 423 K. The resistivity of all crystals decreases with increasing sulphur content (Patel *et al.,* 2008). In the anisotropic ZrS_xSe_{3-x} compounds, the velocity of acoustic wave propagating in a direction parallel to the fibers decreases linearly as the selenium content is increases for $0<x<2$ (Poirier *et al.,* 1985).

Looking to the importance of thermoelectric power generation, it is worthwhile to carry out a systematic study of the thermoelectric properties of semiconducting materials. In this context, authors have put their efforts in carrying out a similar study for the single crystal of zirconium sulphoselenide. In this paper, they have systematically reported about the measurements of thermoelectric power of the as grown crystals of zirconium sulphoselenide as a function of temperature.

MATERIALS AND METHODS

The single crystals of zirconium sulphoselenide (ZrS_xSe_{3-x}) were grown by chemical vapour transport technique with iodine as a transporting agent. A highly pure compound of zirconium powder (97% make: Riedel-de Haen), sulphur (99.97% make: Chiti-Chem Corporation, India) and selenide (99.98% Make: Aldrich, USA) were taken in a stoichiometric proportion in the quartz ampoule for charge preparation. It was evacuated to a pressure of 10^{-5} torr and then sealed. This sealed ampoule was introduced into a two-zone furnace at a constant reaction temperature to obtain the charge. During the synthesis the temperature was slowly increased up to 1073 K with 10 K/h. The ampoule was kept at this temperature for 4 days. Then the furnace was slowly cooled (20 K/h) and brought to room temperature. The resulting brown and/or reddish charge was obtained in the ampoule. This charge was crushed and transferred to other quartz ampoule. The iodine (2mg/cc) as a transporting agent was taken in glass capillaries. These capillaries were kept in the quartz ampoule and evacuated it with 10^{-5} torr pressure. This ampoule was placed in a dual zone horizontal furnace for 10 days at high temperature with a maintaining 50K temperature gradient. After then furnace was cooled up to room temperature with a rate of 10 K/hr. The entire material (charge) got converted into the crystals at the cooler end of the ampoule. The grown crystals were collected after breaking the ampoule. The optimum condition for crystal growth and physical parameters for as grown crystals are shown in **Table1**.

For Hall effect measurements, four contacts were taken on the surface of thin crystals using silver paste and fix it on PCB. This PCB was kept in a known magnetic filed produced by an electromagnet (Type EMPS-5, Omega Electronics, Jaipur, India). The Hall voltage was measured between the two diagonally opposite contacts by passing current through the remaining diagonal contacts.

The thermoelectric power measurements for all the samples were carried out in temperature range of 303 K to 773 K with the help of thermoelectric power measurements setup. It consists of two blocks: (1) Sample holder with heater and pick up probes and (2) Electronic circuit controlling temperature and temperature gradient across the sample.

The sample holder consists of two low power heaters *A* and *B*. The temperature *T* of the heaters *A* and *B* are measured by K type thermocouples (TC_1 and TC_2). The sample under investigation is mounted directly on the heaters, and is held by two pick up probes, which are of copper. These probes also measure the Seebeck voltage developed across the two ends of the sample.

The second block consists of temperature indicator, proportional controller and two-heater control circuit which drive the two heaters *A* and *B*. With the help of this electronic control circuit it is possible to generate a stable temperature gradient between the two heaters. It is possible to control the temperature from 298 *K* to 573 *K* with ΔT of ± 5 *K* simultaneously with better than ± 1 *K* stability. The problems usually encountered in making thermoelectric power measurement are stray thermal emf. The sample and the

electronic circuit have been incorporated into one unit. Use of low power heaters and electronic controllers makes the operation very easy and Seebeck coefficient of the sample can be measured very conveniently.

RESULTS AND DISCUSSION

The optimum conditions for growth of zirconium sulphoselenide single crystals are presented in Table 1. From this Table 1 it is clear that the time required for the growth of these crystals is same but the required temperature increases as the sulphur content increase from $ZrSe_3$ to ZrS_3. The reason for this is the high resistivity of sulphur element.

In Hall effect measurements, the mobility of charge carriers is evaluated using the relation;

$$\mu_H = \frac{t}{\Delta B} \times \frac{\Delta R}{\rho}$$

The Hall coefficient (R_H) and carrier concentration (η) are evaluated using the formula;

$$R_H = \mu_H \times \rho$$

$$\eta = \frac{1}{R_H \cdot e}$$

From the sign of the Hall coefficient, the nature of charge carriers in the grown crystals can be ascertained. All the results obtained from the Hall effect measurements are given in Table 2. The negative sign of Hall coefficient clearly indicate that all crystals are n-type nature and majority carriers in them are electrons.

The measurement of thermoelectric power as a function of temperature is one of the important method for investigating electronic properties of solids. The thermoelectric power (S) provides useful information about the mechanism of electrical transport. As pointed out the quantity S can be used to determine the mobility ratio, the concentration of carriers, the position of Fermi level etc. in addition, the sign of S indicated the type of dominant carriers or the type of dominant electronic conduction. For the study of temperature dependent thermoelectric power 'S' of a p-type semiconductor the following expression (Mohanchandra K P and Uchil J 1997) can be used.

$$S = \frac{k}{e}[A + \frac{E_F}{kT}]$$

where k is Boltzman constant, e is the electronic charge, A is the constant determined by the dominant scattering process and E_F is the separation of the Fermi level from the top of the valance band.

For a small temperature range, E_F is fairly constant and hence if the thermoelectric power (TEP) is plotted against the reciprocal of temperature, a straight line is expected. **Figure 1** shows the variation of TEP with an inverse of temperature for zirconium sulphoselenide single crystals. The values of E_F and A were determined from the slope and intercept respectively, and listed in Table 5 for each samples.

The values of constant 'A' is given by

$$A = 5/2 - s \quad (1)$$

where 's' is the scattering parameter

Revolinsky and Beernsten (Perluzzo G. et al. 1980) express the thermoelectric power,

$$S = \frac{k}{e}[A + \ln \frac{N_A}{\rho}] \quad (2)$$

where N_A is the effective density of states and is given by

$$N_A = 2\left[2\pi m_e^* kT/h^3\right] \quad (3)$$

where m_e^* is the effective mass of electrons. Using the values of carrier concentration obtained from the Hall effect measurement, the effective density of state N_A for the as grown crystals can be calculated with the help of the formula

$$\rho = N_A \exp\left(-E_F/kT\right) \quad (4)$$

where E_F is the Fermi energy and T is the room temperature. The values of effective density of state thus obtained are shown in **Table 3** for all grown crystals.

Using these values of effective density of state, the effective mass of electron for zirconium sulphoselenide single crystals was calculated and presented in **Table 3**. The observed temperature dependence of the thermoelectric power can qualitatively be explained by the analysis of the magnitude of dS/dT with respect to temperature. Differentiation of equation for 'S' with temperature gives

$$\frac{dS}{dT} = -\frac{k}{e}\left[\frac{dA}{dT} + \frac{1}{k}\left(\frac{dE_F}{dT}\right) - \frac{E_F}{kT^2}\right] \quad (5)$$

Table 1. Growth parameters of ZrS_xSe_{3-x} single crystal grown using chemical vapour transport technique.

Sample	Reaction Temperature (K)	Growth Temperature (K)	Physical characteristics of the crystals			
			Growth time (hr)	Plate area (mm^2)	Thickness (mm)	Color & appearance
$ZrSe_3$	1023	973	240	20	0.09	Gray shining
$ZrS_{0.5}Se_{2.5}$	1043	993	240	15	0.09	Black shining
$ZrSSe_2$	1063	1013	240	13	0.08	Black shining
$ZrS_{1.5}Se_{1.5}$	1083	1033	240	15	0.07	Silver black shining
ZrS_2Se	1103	1053	240	11	0.07	Red shining
$ZrS_{2.5}Se_{0.5}$	1123	1073	240	10	0.06	Red shining
ZrS_3	1143	1093	240	10	0.06	Red shining

Table 2: The values of Hall coefficient, mobility and carrier concentration for zirconium sulphoselenide single crystals

Sample	Resistivity ρ (Ω·cm)	Conductivity σ $(\Omega\cdot cm)^{-1}$	Hall coefficient R_H $(cm^3/coul)$	Mobility μ (Cm^2/Vs)	Carrier concentration N (cm^{-3})
$ZrSe_3$	0.67	1.47	-760	1121.6	8.21×10^{15}
$ZrS_{0.5}Se_{2.5}$	0.78	1.28	-895	1145.7	6.97×10^{15}
$ZrSSe_2$	1.20	0.83	-1310	1088.9	4.76×10^{15}
$ZrS_{1.5}Se_{1.5}$	1.68	0.59	-1970	1072.6	3.16×10^{15}
ZrS_2Se	2.85	0.35	-3250	1138.2	1.92×10^{15}
$ZrS_{2.5}Se_{0.5}$	6.69	0.15	-7520	1123.3	0.83×10^{15}
ZrS_3	8.39	0.12	-9500	1132.9	0.66×10^{15}

Figure 2 shows the variation of dS/dT with temperature for single crystals of zirconium sulphoselenide. In the temperature range in which the measurement of 'S' is made, E_F is nearly

constant and so the term dE_F/dT gives a zero contribution and the term dA/dT is negligible and so the variation of dS/dT is controlled by the term E_F/kT^2. If the higher temperature range in which 'S' is measured is increased further then the contribution of E_F/kT^2 will diminish due to the presence of T^2 in the denominator and dS/dT will then be controlled by the term $\frac{1}{k}\left(\frac{dE_F}{dT}\right)$.

Kelvin used the principles of classical thermodynamics to show that the three thermoelectric parameters namely S (Seebeck Co-efficient), μ_T (Thomson Co-efficient) and π (Peltier Co-efficient) are not independent and that only one is needed to specify the other two. He derived the following relations, commonly known as "Kelvin Relation"

$$\mu_T = T\left[\frac{dS}{dT}\right] \tag{6}$$

$$\pi = TS \tag{7}$$

where 'T' stands for temperature.

Although the laws of classical thermodynamics are not directly applicable to thermoelectricity, the Kelvin relation stand the test of experiments extremely well. Since 'S' is known to us as a function of temperature, μ_T and π were evaluated at different temperature for all samples of zirconium sulphoselenide and are plotted in Figure 3 and Figure 4 respectively.

Table 3: The values of the Seebeck parameters for zirconium sulphoselenide single crystals

Sample	A	Scattering parameter 's'	Fermi energy 'E_F' (eV)	Effective mass of electron m_e^* (m_e)	Effective density of state 'N_c' (cm^{-3})
$ZrSe_3$	0.69	1.81	0.013	0.0102	1.31×10^{16}
$ZrS_{0.5}Se_{2.5}$	0.79	1.71	0.014	0.0095	1.19×10^{16}
$ZrSSe_2$	1.12	1.38	0.022	0.0090	1.11×10^{16}
$ZrS_{1.5}Se_{1.5}$	1.35	1.15	0.027	0.0078	0.89×10^{16}
ZrS_2Se	1.71	0.79	0.038	0.0075	0.83×10^{16}
$ZrS_{2.5}Se_{0.5}$	2.27	0.23	0.056	0.0068	0.72×10^{16}
ZrS_3	2.49	0.01	0.061	0.0066	0.69×10^{16}

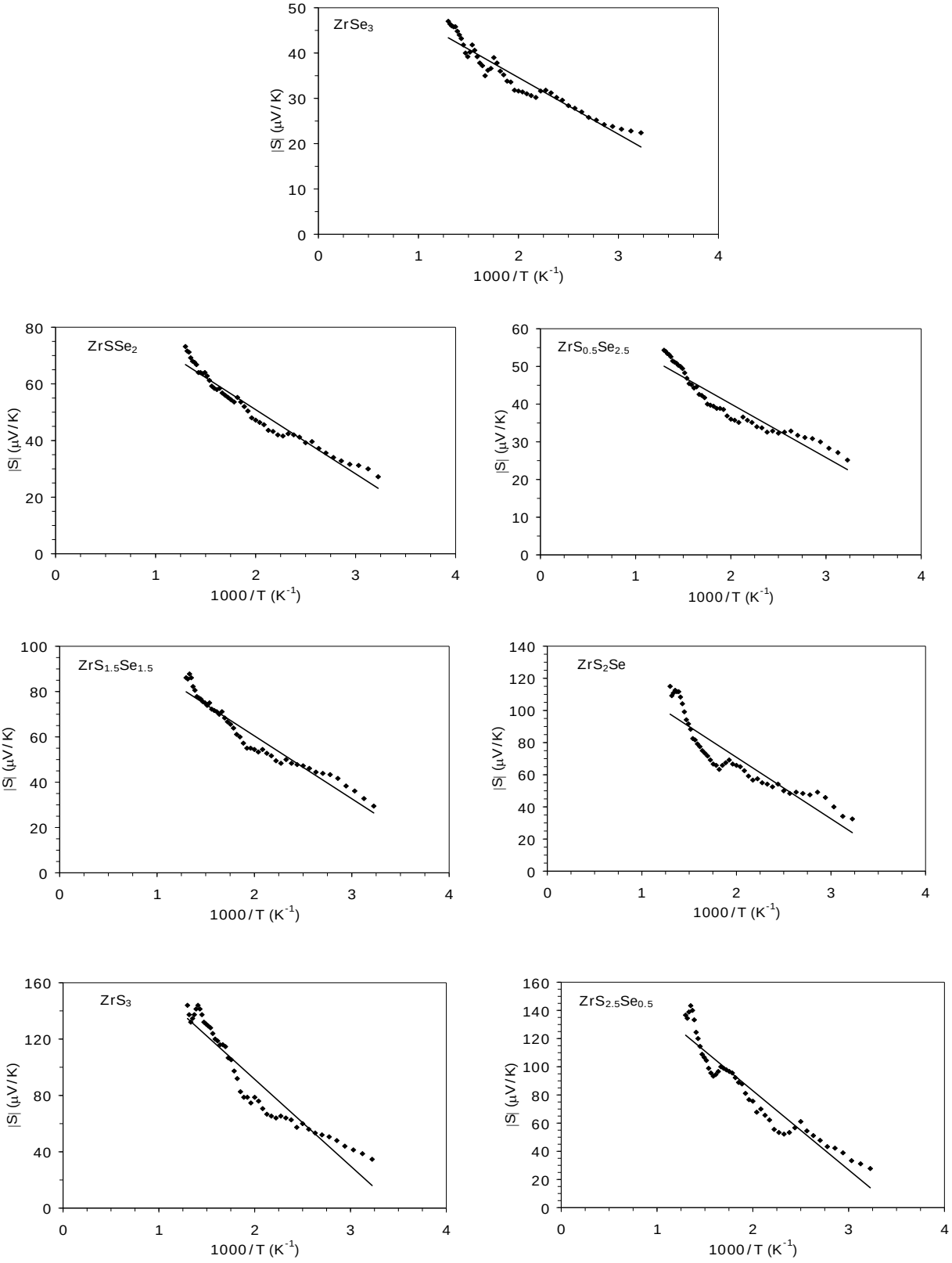

Figure 1: The variation of thermoelectric power with thousand inverse of temperature for zirconium sulphoselenide

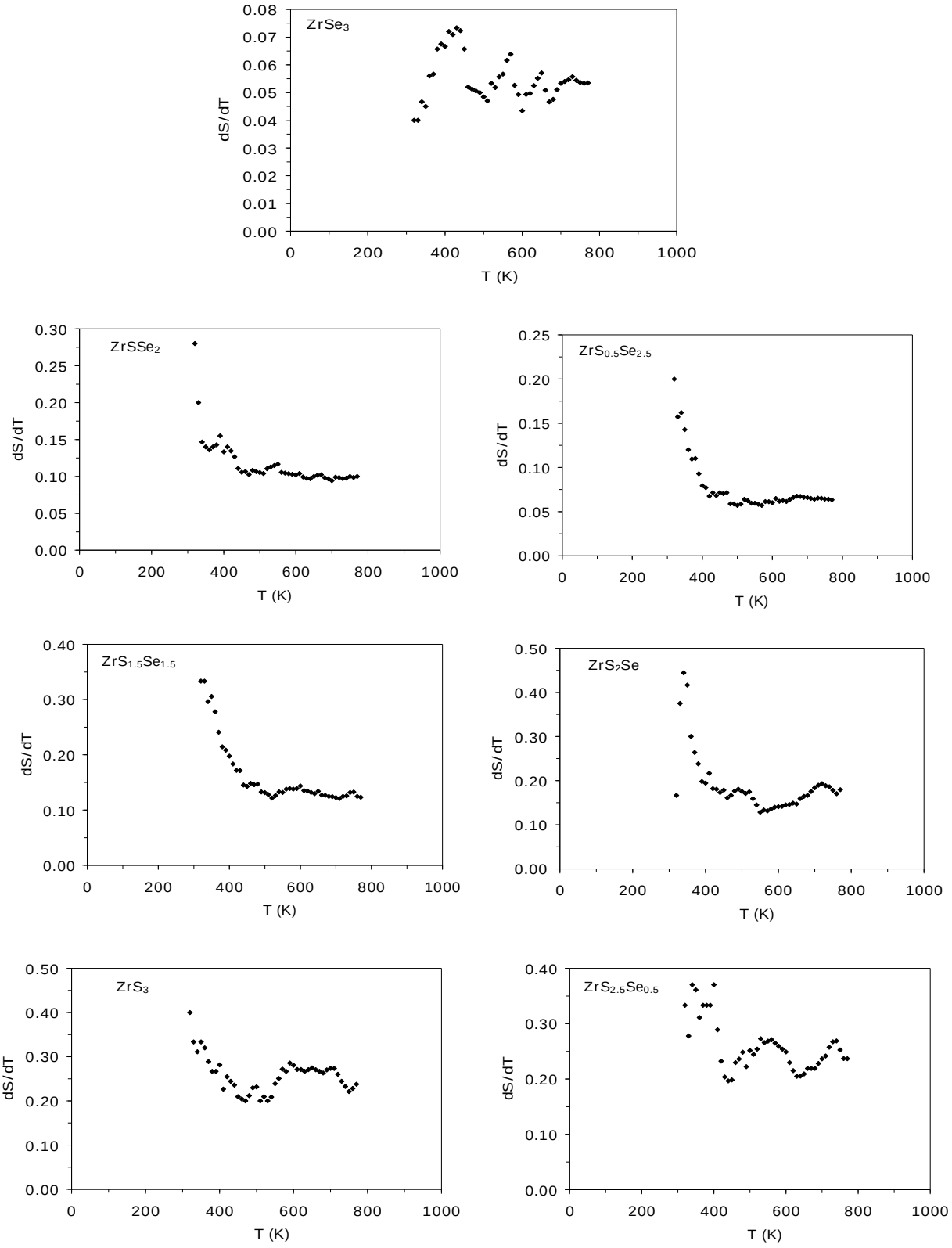

Figure 2 The variation of dS/dT with temperature 'T' for zirconium sulphoselenide single crystals

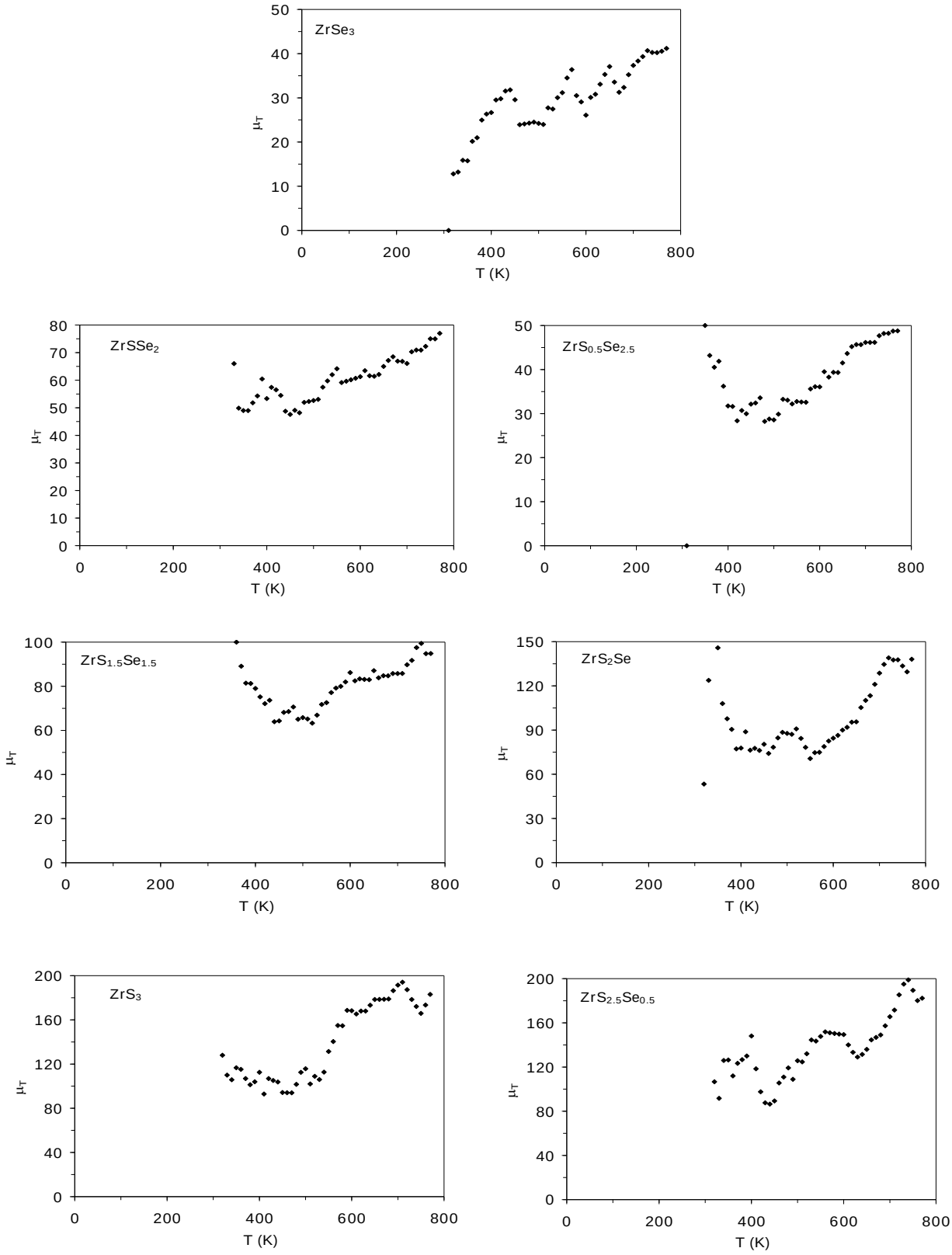

Figure 3: The variation of Thomson Co-efficient (μ_T) with temperature 'T' for zirconium sulphoselenide single crystals

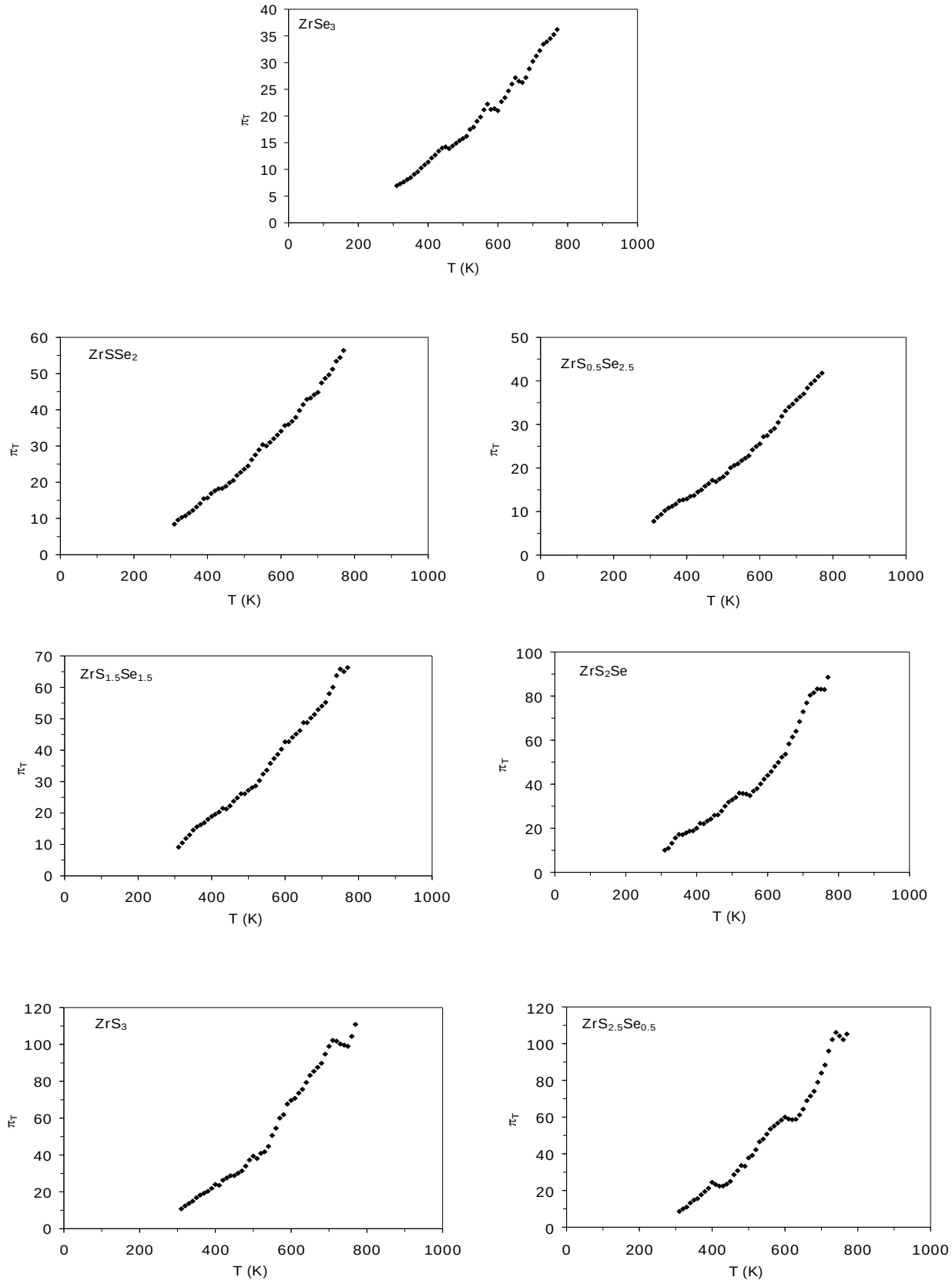

Figure 4: The variation of Peltier Co-efficient (π_T) with temperature 'T' for zirconium sulphoselenide single crystals

The sign of thermoelectric power (TEP) in the semiconducting phase decide the type of majority charge carriers. The fact that TEP in ZrS_xSe_{3-x} is negative clearly indicates that these crystals are n-type semiconductor. Further in all cases there is no change in sign of TEP with an increase in temperature. This suggest that materials does not undergo any phase transition in the entire temperature rang studied. The n-type nature of the samples supports the conclusions drawn from the Hall effect measurement. The room temperature value of thermoelectric power increases with increase in the value of 'x' in ZrS_xSe_{3-x}. It is well know that large 'S' suggests that the material is close to stoichiometric composition. The increase in the value of 'S' with increase in 'x' in ZrS_xSe_{3-x} makes the crystals more resistive and more close to stoichiometric composition.

Figure 3 and **Figure 4** shows how does Thomson co-efficient and Peltier co-efficient varies with temperature for as grown crystals. The significant observation can be made from these figures that at higher temperature all crystals behave likes intrinsic semiconductor. The Peltier co-efficient π plays an important role when a p-n junction is formed and a relatively large amount of heat is evolved.

As it is well known that the thermoelectric coefficient plays an important role in calculating the figure of Merit given by

$$Z = \frac{S^2}{\rho} k_T \qquad (8)$$

where 'S' is Seebeck co-efficient and 'ρ' is resistivity and k_T is thermal conductivity.

The values of figure of Merit give the importance of material to be used for thermoelectric devices. Therefore it is necessary to deduce optimum values of 'S' corresponding to maximum values of figure of Merit. Since 'S' enters the figure of Merit as square, great care must be taken to reduce the magnitude of error of measurement. Since the optimum values of 'S' for a material to be used in thermoelectric devices should be $\cong 200\mu V/°K$ at room temperature, henceforth zirconium sulphoselenide is nearly coming in this range and therefore this material can be tried for calculating "Z" i.e. figure of Merit and probably can serve as a thermoelectric material.

Conclusion

A study of the results reveals that

1. The negative sign of Hall co-efficient reveals that all grown crystals are n-type in nature and majority charge carriers in them are electrons, which confirms the nature obtained by TEP measurement.

2. It is seen that in all cases thermoelectric power increases linearly with increasing temperature confirming the typical semiconducting behaviour of all crystals.
3. The variation of thermoelectric power with temperature shows that the charge impurity scattering predominates in zirconium sulphoselenide single crystals.
4. The reduction in effective mass of electrons with increase in sulphur content in ZrS_xSe_{3-x} single crystals is in agreement with the decrease in carrier concentration and increase in resistivity.
5. The observed temperature dependence of thermoelectric power has been qualitatively explained.

REFERENCES

Furuseth S, Brattas L and Kjekshus A, Acta chem. Scand. **A 29**, 623 (1975)

Ikari T, Provencher R, Jandl S and Aubin M 1983. Electrical properties of vapour grown $ZrSe_3$ single crystals, Solid State Commun. **45 (2)** 113

Caillat T, Fleuriel J P and Borshchevsky A 1997. Preparation and thermoelectric properties of semiconducting Zn_4Sb_3, Journal of Physics and Chemical Solids, **58 (7)** 1119

Brattas L and Kjekshus A, 1972. On the Properties of Compounds with the ZrSe3 Type Structure. Acta Chem. Scand. **26** 3441

Lee P, Said G and Davis R 1969 Negative resistance and switching effect in the single crystal layer compounds SnS_2 and ZrS_2, Solid State Communication **7** 1359

Tributsch H 1981 Photoelectrochemistry of Layer-Type Zirconium Disulfide, Journal of Electrochemical Society **128** 1261

Patel Kaushik, Prajapati Jagdish, Vaidya Rajiv and Patel S. G., 2005. Optical and electrical properties of $ZrSe_3$ single crystals grown by chemical vapour transport technique, Bulletin of Material Science **28 (5),** 405

Patel Kaushik, Prajapati Jagdish, Vaidya Rajiv and Patel S. G., 2005. Study of optical and electrical properties for ZrS_3 single crystals, Indian Journal of Physics 79 **(4),** 373

Patel K R, Vaidya R D, Dave M S and Patel S G Patel 2009. Growth and high-pressure studies of zirconium sulphoselenide single crystals, Pramna Journal of Physics, 73(5) 945-953

Patel K R, Vaidya R D, Dave M S and Patel S G Patel 2008. Crystal growth and structural analysis of zirconium sulphoselenide single crystals, Bulletine of Material Science 31 (4) 645-654

Poirier M. and Seguin P. E., 1985. Acoustic properties of $ZrS_{3-x}Se_x$ compounds, Solid state communications **54(5)** 375

Mohanchandra K P and Uchil J, 1997,Thin Solid Films, **305** 124

Perluzzo G., Lakhani A. A. and Jandl S., 1980 Electrical transport measurements in a quasi-one dimensional semiconductor ZrS_3, Solid State Communication., **35** 301