Growth and electrical properties of ternary ZrSTe crystals

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We reports new ternary ZrSTe crystals gown by chemical vapour transport method. Vapor transport experiments with iodine were performed on the system ZrSTe to define optimum growth conditions in terms of crystal size and surface perfection. Confirmation of stoichiometric proportion of constituent elements of grown crystals was done by Energy Dispersive Analysis of X-rays (EDAX). To find out resistivity we have performed two probe resistivity measurements and Hall coefficient, mobility as well as carrier concentration are obtained by Hall effect measurements along the cleavage plane of as grown ZrSTe crystals. Preliminary electrical resistivity measurements show a decrease of the resistance with temperature which suggests a semiconducting nature of ZrSTe. We also report thermoelectric power of ZrSTe crystals in temperature range 313K-573K. Data of Hall coefficient and thermoelectric power have good agreement with available data and confirms the semiconducting behavior as well as n-type nature of ZrSTe crystals. This finding will inspire the search for similar materials and promote an in-depth investigation of the detailed operating mechanism.

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1. Introduction

Most of the technological, electronic and optoelectronic applications utilize semiconductor material in crystalline forms [1]. Here we have grown

ZrSTe crystals by chemical vapour transport method using dual zone horizontal furnace. This technique has been used for the growth layer compound by various research groups [2-4]. Stochiometric proportion of prepared compound was confirmed by energy dispersive analysis of X-rays. Solid material that exhibits some physical properties nearly invariant over a substantial temperature range can be very useful for the applications [5]. Electrical resistivity is a physical property of enormous importance, both for the understanding of the solids and their actual applications. The electrical resistivity of solids, apart from the possibility of superconductivity, can vary in the range of 10^{32} which may be the widest of any common physical properties of solids [6]. Moreover, the temperature dependence of the electrical resistivity behaves quite irregular, since various mechanisms, including the phonon scattering, impurity and defect scattering, mutual scattering of electrons, and so forth, are involved in the electrical transport in different temperature ranges [6-7]. Resistivity measurements and Hall Effect measurements were performed in order to determine resistivity, conductivity, mobility and carrier concentration along the basal plane of as grown ZrSTe crystals. The thermoelectric effect offers a distinctive advantage over other methods because the measured thermoelectric voltage is directly related to the carrier concentration, which makes the thermoelectric measurements simpler even for high mobility materials [8]. The study of thermoelectric power provides an independent way to determine the carrier sign, density and position of Fermi level in semiconductors [9]. Thus the aim of this work is to report the growth parameters and to explain the transport properties of ZrSTe crystals.

2. Experimental

2.1Crystals growth

With a view to allowing effective and faster transport of constituents to produce the necessary super saturation for crystal growth in a vapor phase system, the chemical (iodine) vapor transport method was employed for the growth of ZrSTe. A mixture of elements 99.99% Zr, 99.99% S and 99.99% Te, according to the information supplied by manufacturer Alfa Aesar was taken in a quartz ampoule of length 26cm and a diameter of 2.50cm along with an iodine capillary. The ampoule was slowly cooled, evacuated to around 10^{-3} Torr and sealed off. The ampoule was placed in the dual zone horizontal furnace controlled by temperature controller with an accuracy of ±1 K. A reverse temperature profile was developed across the ampoule over several hours to get cleaning effect on the quartz walls of the growth zone. The duration was 27 hours. After this, the temperatures of source zone and growth zone were maintained at 973K and 873K, respectively. The duration of growth was 75 hours, and then, the furnace was slowly cooled at the rate of about 60 K/h up to 323K. The long needlelike ZrSTe single crystals

were obtained. The crystals were metallic gray in color with maximum length of 9mm shown in Fig. 1. The chemical composition of the grown crystals was studied through Energy Dispersive Analysis of X-rays (EDAX). The result of Energy Dispersive X-rays Spectroscopy (EDS) is shown in Fig. 2.

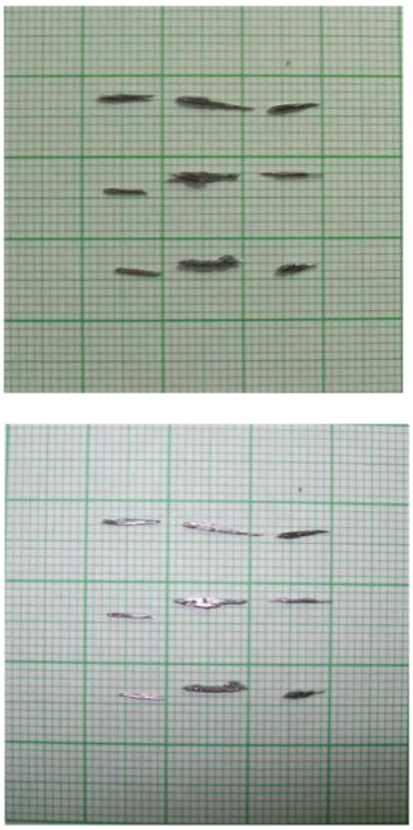
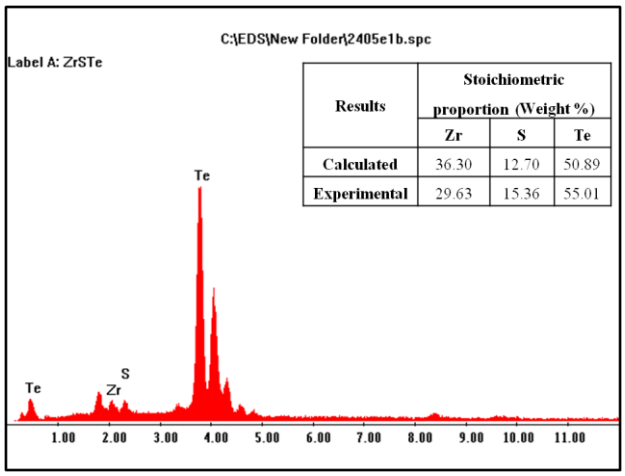


Fig. 1. Photograph of ZrSTe single crystals.



Results	Stoichiometric proportion (Weight %)		
	Zr	S	Te
Calculated	36.30	12.70	50.89
Experimental	29.63	15.36	55.01

Fig. 2. EDS of ZrSTe crystals.

2.2 Electrical properties measurements

2.2.1 Resistivity measurements

The temperature dependence of the electrical conductivity for solids is susceptible to many influencing factors; no hard-and-fast rules are available. For a semiconductor, the electrical conductivity can be formally written as $\sigma=e(n_e\mu_e+ n_h\mu_h)$, where e and h denote electron and hole, while n and μ stand for the carrier density and carrier mobility, respectively. Both the carrier mobility and the carrier density, or the number of the carriers, are temperature dependent [10], yet the temperature dependent electrical conductivity is dominated by that of the latter, since the mobility changes only in a mild way with the lattice temperature while the number of carrier can be an exponential like function of 1/T. with decreasing temperature, the number of the carriers decreases while the mobility generally increases, [6, 10].

The electrical resistance measurements along the cleavage plane of grown crystals were carried out in the temperature range from 308 K to 573 K at an interval of 5 K. The resistivity of the samples was calculated by using the formula

$$\rho = \frac{RA}{l}$$

Where A is the cross section area of the specimen in the direction of measurement, R is the resistance of the specimen and l is the length of specimen. Figure 3 shows the variation of resistivity as a function of temperature. Sample exhibit semiconducting behavior: resistivity increases with increasing temperature reaches its maximum value and then decreases. From the slopes of lnσ Vs 1000/T plots the values of activation energies were calculated using the formula,

$$E_a = 2.303 \times k_B \times 10^3 \times \text{slope (eV)}$$

Where $k_B = 8.602 \times 10^{-5}$ eV/K

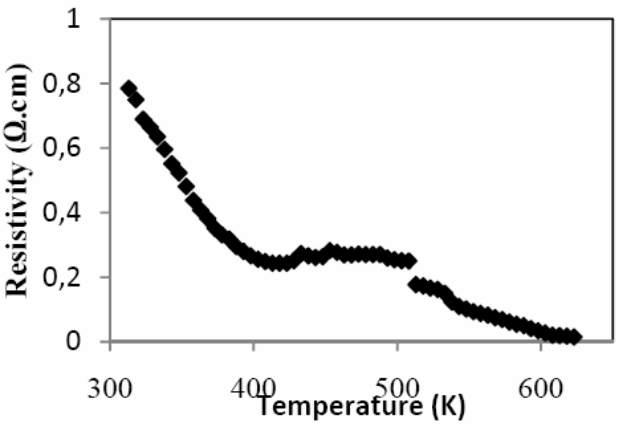


Fig. 3. Graph of resistivity vs. temperature for ZrSTe single crystals.

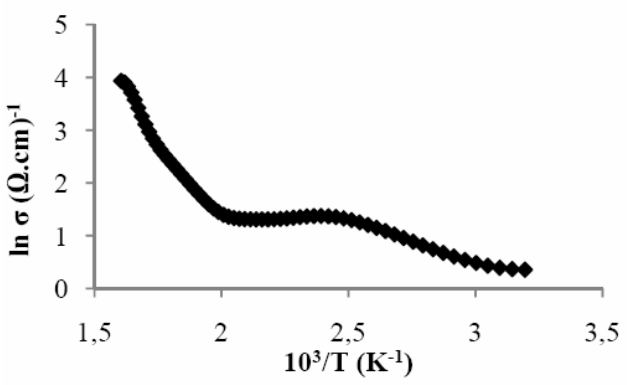


Fig. 4. Graph of ln σ Vs 1000/T for ZrSTe single crystals.

2.2.2 Termoelectric power measurements

The measurements of the thermoelectric power (TEP) with temperature were carried out in the temperature range 308K to 573K.

For the study of temperature dependent thermoelectric power S of a semiconductor the expression is given by [11-12].

$$S = \frac{k_B}{e}[A + \frac{E_{FV}}{k_B T}]$$

Where k_B is Boltzmann constant, e is the electronic charge, $E_{FC} = E_F - E_C$ is the separation of the fermi level from the bottom of the conduction band and A is the constant determined by the scattering process and is defined as

$$A = 5/2 - s$$

Where *s* is scattering parameter

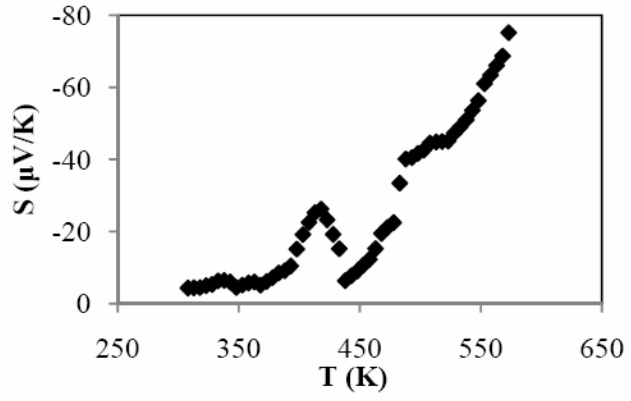


Fig. 5. Graph of Thermoelectric power S vs. temperature for ZrSTe single crystals.

2.2.3 Hall effect measurements

Hall effect measurements were performed along the cleavage plane of as grown crystals ZrSTe in order to determine the conductivity type, mobility and carrier concentration using the formulas;

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

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

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

Where, *n*= carrier concentration
R_H= Hall coefficient,
μ_H=Mobility
t= thickness of the sample
ρ= Resistivity of the sample

3. Results and discussion

The long needlelike single crystals of ZrSTe grown with the growth zone temperature of 873 K are shown in Fig. 1. Growth parameters were described in the preceding section. The crystals nucleation rate depends on the magnitude of super saturation of the gas phase, which is proportional to the temperature difference between the source zone and the growth zone [13]. In our experiment, the temperature gradient between source and growth zones was 100 K. From the result of Energy Dispersive X-rays Spectroscopy, it is confirmed that the chemical composition of ZrSTe is in good agreement with the calculated data which are shown in the inset of Fig. 2. The resistivity along the cleavage plane decreases with increase in the temperature which indicates the semiconducting behavior of the as grown crystals which is shown in Fig. 3. Samples exhibit semiconducting behavior: resistivity increases with increasing temperature, reaches its maximum value and then decreases. Typical data presented in Fig. 4 shows that the conductivity as a function of temperature in the range 313-623 K. The curve is quite similar to the simple semiconductor behavior. It should be noted that in the curve in Fig. 4, three regions can be distinguished. Beginning from the low temperature, the electrical conductivity (σ) increased slowly with temperature, and this is due to the fact that the carrier concentration in this region is determined by the number of ionized donor liberated from the impurity level. From this region the activation energy was calculated, indicating that the donor level lies at 0.12 eV below the bottom of the conduction band. The σ–T curve passes through an intermediate region, 408-473 K. This is the transition from impurity to intrinsic conductivity which depends on the carrier concentration and their mobilities. At the temperature above 473 K, the conductivity increases rapidly because of carrier being excited from the valence band into extended state of conduction band. So the width of forbidden energy gap can be calculated. It is found to be 1.38 eV. At low temperature electrical resistivity is a characteristic of extrinsic conduction, while at higher temperature the number of carriers thermally excited across the semiconducting energy gap begins to overwhelm the number of carriers due to ionized impurities and the intrinsic conduction begins to

predominate. The electrical resistivity maximum is shifted to higher temperatures with increase in carrier concentration [14]. In the high temperature range (T >493K), the carrier scattering mechanism is the scattering on thermal lattice vibration, which causes the mobility decreases with the temperature increase. The mobility decreases according to the law $\mu \alpha T^{-7.2}$ [9]. This leads to assumption that phonon scattering is dominant.

The result for the temperature dependence of TEP of single crystals ZrSTe in the temperature range 308-573 K is presented in Fig. 5. At the beginning of the curve TEP increases as the temperature rises, reaching the value at S equal to -27 μVK^{-1} at T = 418 K. A sharp drop of TEP is observed until it reaches -6 μVK^{-1} at T = 438 K. The decrease of S values, at the temperature higher than 418 K, is regarded as a temperature of compensation processes [15]. Above the 438 K the TEP increases with increasing temperature. The observed negative values of thermoelectric power in the entire investigated temperature range follows from the fact that the electron concentration is greater than that of hole, that is, the material is n-type. This agrees with result obtained from Hall effect data. So this result is quite logical. Negative sign of Hall coefficient and Seeback coefficient indicates that crystal ZrSTe is n-type in nature and majority carriers in them are electrons. From the variation of thermoelectric power with temperature gives the value of scattering parameter and fermi energy are given in Table 1. All the results obtained from the Hall Effect measurements are given in Table 2.

Table 1. Value of the parameters A, E_{FV} and s for ZrSTe single crystals.

Parameter	ZrSTe
A	1.356
E_{FV} (eV)	0.69
s	1.144

Table 2. Hall parameters for ZrSTe single crystal.

Parameter	ZrSTe
Resistivity x 10^{-2} (Ω.m) at room temperature	0.8027
Hall Coefficient x 10^{-6} (m^3 $coloumb^{-1}$)	-6680
Type	N
Mobility x 10^{-4} (m^2/V.s)	257.006
Carrier concentration x 10^6 (m^{-3})	3.92 x 10^{15}

4. Conclusion

In the present paper, the growth, Energy Dispersive X-rays Spectroscopy, electrical conductivity, Hall effect and thermoelectric power of ZrSTe are reported. Different growth runs were carried out for the growth of ZrSTe single crystals by CVT technique using iodine as a transporting agent. This work revealed that crystalline zirconium-sulfur-telluride has a semiconducting nature with n-type conductivity. It has a forbidden energy gap of 1.38 eV and activation energy of donor of 0.12 eV. Investigation of the dc electrical conductivity, Hall effect and thermoelectric power data allows us to deduce many important parameters such as the mobility, resistivity, Hall coefficient, carrier concentration, and scattering parameter. The scattering mechanism of the charge carriers was discussed in the present study. This mode of investigation (crystal growth and thermoelectric properties study) is an ideal way for finding out the possibility of making applications for these semiconductor compounds especially in the field of energy conversion, semiconductor devices and electronic engineering.

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