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Short Communication

THERMOELECTRIC POWER (TEP) OF LAYERED CHALCOGENIDES GaTe CRYSTALS

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TEP measurements of gallium mono-tellurite single crystals have been studied over the temperature range 193–583 K. GaTe single crystals grown from melt by the modified Bridgman technique method. The results of measurements indicate that the investigated samples turned out to be P-type nature. Investigation of GaTe compound revealed that it has interesting properties. Many physical parameters were determined such as carrier mobilities, effective masses of free charge carriers, diffusion coefficient and diffusion length as well as the relaxation time. The highest value of figure of merit for GaTe permit the practical application as thermoelectric element.

Keywords: *chalogenide, GaTe, semiconducting compounds, single crystals, thermoelectric power*

Introduction

GaTe is a A^{III} B^{VI}-type semiconducting compound like GaSe, GaS and InSe, which crystallize in a layered structure. Mainly, due to the difficulties in growing good quality large size crystals, it is one of the less investigated materials. In the case of GaTe, atomic planes are in the Te–Ga–Ga–Te sequence, grouped in layers of four atomic planes where portions of each layer are joined together by regions in which the Ga–Ga bonds are approximately at right angles to the usual Ga–Ga bonds [2]. The anisotropy arises from the fact that the bonding within the layers is considerably stronger than those perpendicular to them. In GaTe, Van der Waals forces contribute predominantly to the interlayer interaction while the bonding forces within the layers are primarily ionic-covalent. Gallium–tellurium is a binary alloy system which sexhibits anomalous physical and chemical properties [3]. Studies undertaken for the establishment of the equilibrium diagram of the gallium tellurium system proved the existence of the equiatomic compound GaTe which is formed by eutectic reaction at 1109 K. The monoclinic lattice [4] of GaTe as a space symmetry group where a=11.95 Å, b=4.04 Å and c=14.82 Å. Most published works presented in the literature are interested in studying the crystal structure [4–6] visible reflection spectra [7], the photoconductivity spectra [8] the anisotopy in the absorption spectrum at the fundamental edge [9] also the electrical conductivity and Hall effect [10, 11] photoluminescence characterization [12], Raman spectral [13], memory switching [14] and other physical properties [15], thermoelectric properties have not been catalogued in the literature. However no information at all was published on thermoelectric power of GaTe as far as we know. In view of this the present work aims to investigate the thermoelectric properties which is essential to the understanding of the material and consequently their application in energy conversion devices.

Experimental

Sample preparation

GaTe single crystal was grown from melt using Bridgma technique in the solid-state laboratory at Girls colleges of Education in Jedda Saudi Arabia.

Special design was used for crystal growth, which is a part of the UNESCO program for locally produced equipment for physics research. In this design it demonstrates that the driving force required to move the loaded silica ampoule is equivalent to the decrease of the water level drained in a special container which in turn indicated the rate of motion. The sample was prepared from high-purity gallium (6N)

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representing 64.656% and tellurium (5N) representing 35.3439% the principle of the design and details of the process were published previously [16]. Samples obtained were single crystals of good quality and they were brittles showing a layer structure. The crystal perfection was checked using the X-ray diffraction technique. Diffraction for these materials compared with the index data of the American society for testing materials (ASTM) cards. From these X-ray studies it was evident that the crystals have a high degree of crystallinity indicating that the preparation technique is farily reliable and satisfactory.

Experimental arrangement

Single crystals samples were prepared by gently cleavage, from the product ingot with the aid of a razor blade. The length of the sample was chosen to be as short as possible, whereas the cross sectional area was large enough. The surface of the sample was flat and parallel. The prepared sample was of a desk shape with diameter 9.8 mm and thickness 3.8 mm. It was necessary to have the temperature equally distributed. Therefore we placed contacts of silver past across the ends of the specimen uniformly. A two-part holder was used for making the temperature difference along the crystal in a direction perpendicular to the natural cleavage plane. The ambient temperature was produced by one of them, but the second heater was electrically energized to have the temperature difference. The sample was insulated from the holders by a thin sheet of mica. The sample was clamped between the two holders gently and introduced inside an evacuated working chamber two well calibrated thermocouples, made of copper constantan, were used for measuring the sample temperature at each end. The temperature of the crystal was considered to be the average of those at its two ends. The temperature difference was kept small (about 5 K). Simultaneous measurements of temperature and potential difference were carried out to increase the accuracy of the measurements. Details about apparatus and experimental method measuring (α) have been described in previous paper [7]. Measurements were carried out, during this investigation in a wide range of temperature extending from 193 up to 583 K.

Results and discussion

The variation of the differential thermoelectric power (α) of GaTe-single crystal as a function of temperature is illustrated in Fig. 1. Results and the figure indicate the following points (1) our sample shows P-type conductivity (2), the figure shows that at the beginning of he curve TEP decrease slowly as the temperature rises till reaching 380 K, after which α decrease rapidly reaches its smallest value 85 μV K^{-1} at 435 K, this may be due to presence of some crystal defects or trapping centers in the direction of the carrier flow. (3) Above 435 K with further rise of temperature, a increases rapidly till reaching α value of about 250 αV K^{-1} corresponding to 583 K. Such behavior is expected in this intrinsic range where generation of both carries (electrons and holes) contributed to the increment of (α) value. In the intrinsic region we can apply the following formula [8]

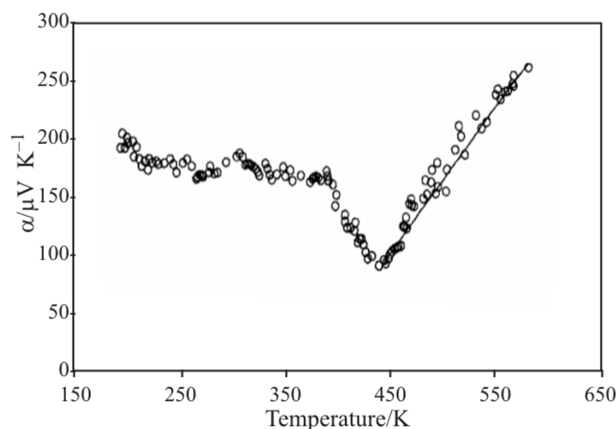

Fig. 1 Temperature dependence of thermoelectric power

$$\alpha = \frac{K}{e}\frac{b-1}{b+1}\left(\frac{\Delta E_{\mathrm{G}}}{2KT}+2\right)+\frac{3}{4}\ln\frac{m_{\mathrm{n}}^{*}}{m_{\mathrm{p}}^{*}}$$

where K is the Boltzman constant, b is the ratio between the electron and hole mobilities m_{n}^{*} and m_{p}^{*} are the effective masses of electrons and holes respectively and ΔE_{g} is the energy gap. In accordance with this equation a plot of α as a function of reciprocal of absolute temperature is a straight line as shown in Fig. 2. The measured thermoelectric power in conjuction with the published hail data [11] is used to calculate the required physical parameters. The slope of the

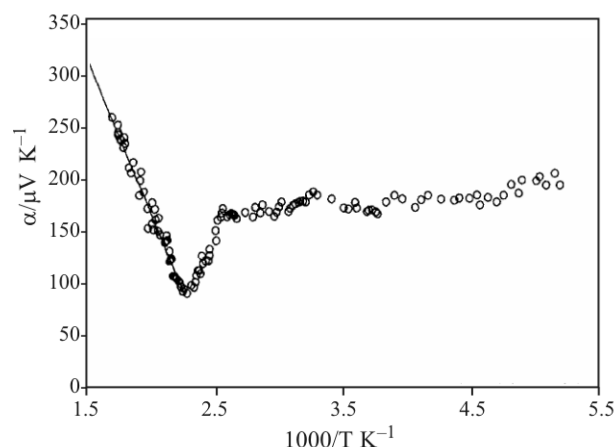

Fig. 2 Relation between α and 1000/T

linear part of the dependence in the intrinsic region is used to estimate the ratio of electron to hole mobilities. Taking ΔE_g=1.6 eV and assuming that m_n^* / m_p^* does not vary with temperature, it can be deduced that $b=\mu_n/\mu_p$=2.268. Since μ_p=12 cm^2 V^{-1} s^{-1}, the electron mobility is found to be 27.216 cm^2 v^{-1} s^{-1}.

The ratio between the effective masses of both electrons and holes can be evaluated from the intersection of the curve, and is found to be m_n^* / m_p^*=2.525·10^{-3}. The diffusion coefficient for majority and minority carriers at room temperature can be estimated and is found to be D_n=0.705 and D_p= 0.311 cm^2 s^{-1}. The relation between α and ln*T* is illustrated in Fig. 3. At low temperature the value of TEP decreases slowly and gradually with temperature. In the transition region a drop of the value of TEP is observed as the temperature increases. In the intrinsic region the value of α increases with temperature calculation of the TEP in the impurity region, yields the following results.

$$\alpha = \frac{K}{e}\left[2 - \ln\frac{ph^3}{2(2\pi m_p^* KT)^{3/2}}\right]$$

where the sign of α is the sign of the charge carrier, *p* represents the concentration of free charge carries (hole) and m_p^* denotes the effective mass of holes. Figure 4 shows the dependence of thermoelectric power on carrier concentration for GaTe sample. As it is shown α decreases linearly with increasing of carrier concentration. Calculation of the effective mass of hole from the intersection of the curve yields consistently the value m_p^*=8.1–9·10^{-29} kg combining this value with the above mentioned result for the ratio *m*/*m*, one can obtain the effective mass of electrons m_n^* / m_p^*=2.047·10^{-31} kg.

Also we deduced the effective masses of holes and electrons related to the rest mass, and the value m_p^*=98*m* for holes and m_n^*=0.225*m* for electron. Since the effective mass values are available, now the relaxation time for both types of carriers can be determined. The relaxation time for holes, as calculated is 6.08·10^{-16} s whereas the relaxation time for electrons equals 3.482·10^{-18} s. It is noticed that the diffusion constant is inversely proportional to the effective mass of the carriers. This is logical because the hole effective mass is larger than that of the electrons.

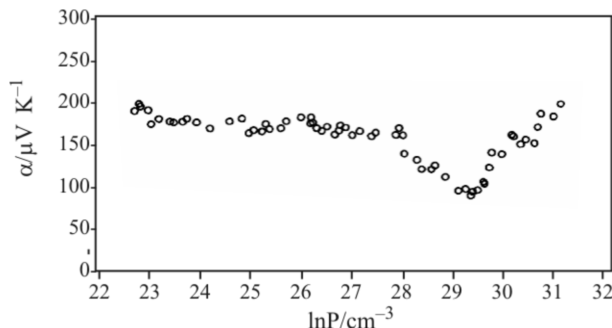

Fig. 4 Relation between α and charge carrier concentration

Also the diffusion length can be established from our data. The diffusion length for holes and electrons are L_p=1.375·10^{-8} cm and L_n=1.567·10^{-9} cm, respectively. Figure 5 represents the relation between TEP and the electrical conductivity. It is seen from the curve that three regions is noticed. The values of α at the first region decreases gradually. At conductivity equal to 1.65·10^{-12} Ω^{-1} cm^{-1} a rapid decrease of α is observed. The value of TEP corresponding to the minimum is about 90 μV K^{-1} at σ=6.68·10^{12} Ω^{-1} cm^{-1} after which TEP increases rapidly as the electrical conductivity continues to increase the behavior of the curve between charge carrier concentration and TEP is similar to that of α *vs.* σ. However, those parameters are found to be sufficient to give a complete information about the general behavior of the GaTe single crystal. The choice of materials for thermocouples, thermoelectric generation, and where α is the differential thermoelectric power and σ is the electrical conduction and *K* the thermal conductivity, refrigerators is based on the efficiency parameter *Z*, defined by the relation $Z=(\alpha^2\sigma)/K$. However the term figure of merit (*Z*) is a measure of both performance and efficiency of a certain thermoelectric element. Therefore the main technical problem to obtain a good thermoelectric element is to answer the question, how to promote the figure of merit of the mate-

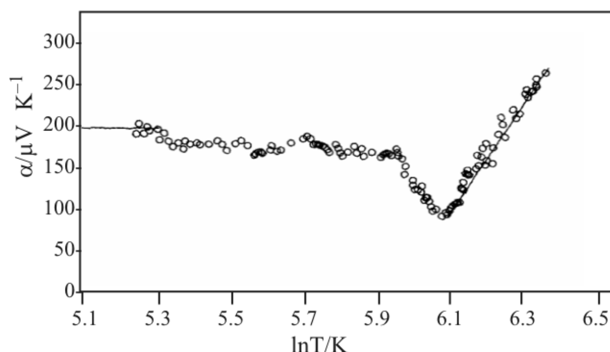

Fig. 3 Relation between α and ln*T*

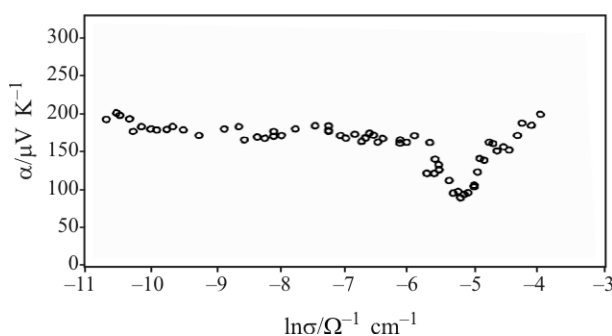

Fig. 5 Variation of α with electrical conductivity

rial. The best material to be used as thermoelectric element is that the highest value of *Z*.

For our best GaTe samples the figure of merit at 300 K equal to Z=37.27 K^{-1}. One determines this value by using the published value of *K* [19] which is equal to 10.1 W K' m'. The highest value of *Z* for GaTe permit the practical application as thermoelectric element.

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