[The Growth and Characteristic features of some compounds of the Ternary Thallium chalcogenide]

Maryam Hamad Salem Alhossainy

Summary

Most of the technological, electronic and optoelectronic applications utilize materials in crystalline formes.
Single crystal semiconductors have important practical applications in technology, For example, much better frequency stability and lower acoustic losses can be better achieved in single crystals than in polycrystalline aggregates.
The interaction of the chalcogenides in the TI_2X-Bi_2X_3 (X= S, Se, Te) systems leads to the formation of ternary chemical compounds with different formal compositions.

$TIBiTe_2$ and TI BiS_2 belong to the family of ternary compounds 111-V-VI_2 (111-TI; V-Sb, Bi; and VI-S, Se, Te) which are characterized as pseudobinary of the type IV –VI. The two members of this of the type TIBi-VI_2 are narrow-gap semiconductors, isoelectronically analogous to the Pb-VI compounds. $TIBiTe_2$ and $TIBiS_2$ possess interesting properties that lead to several applications as optoacoustic detectors, infrared detectors, thermoelectric devices and non-destructive switching and memory elements $TIBiTe_2$ and $TIBiS_2$ belongs to the group of semiconductors with layered structure and are the structural a nalogs to the PbTe and PbS.

In spite of their potential technological uses the investigation of these materials is of interest. For these reasons the subject of this investigation is to prepare $TIBiTe_2$ and $TIBiS_2$ in single crystal form and study the main physical properties, because of their interesting features.

As far as we know from the published literature up to now, there is still insufficient to throw a clear light upon the actual behavior of these compounds. Also some of the results given in the literatures show some discrepancies .

In view of this the present work aims to prepare $TIBiTe_2$ and $TIBiS_2$ in single crystal form and investigate the main physical properties of $TIBiTe_2$ and $TIBiS_2$ single crystal. This study is a timely one in view of the recent interest in these compounds

$TIBiTe_2$ and $TIBiS_2$ single crystal were grown using a special design for crystal growth from melt based on Bridgman technique.

In this study we used slow cooling method. The product ingots were identified with x-ray analysis, the obtained specimens were prepared with the required dimensions for electrical conductivity, Hall effect, thermoelectric power and switching effect measurements. Our investigation gives important results not only to the present thesis, but also for the practical application.

The results of our measurements can be summarized as follows.

1- Electrical conductivity and Hall coefficient :

a-For $TlBiTe_2$ single crystals

An investigation has been carried out on the influence of temperature on the electrical conductivity and Hall effect. The study covers a wide range of temperature extends from 178 K to 568 K.

The energy gap is calculated to be ΔE_g= 0.434 eV the conductivity throughout the entire temperature range is found to be of p-type. The hole mobility at room temperature is of the order μ_H=2.2575x10^3 cm^2/ V.sec. The electrical conductivity at 300K equal 5.0617×10^{-6} Ω^{-1} cm^{-1}.

The carrier concentration at room temperature equal 1.4×10^{10} cm^{-3}. The ionization energy of acceptor as well as Hall coefficient at room temperature was found to be ΔE_a= 0.16 Ev and R_H = 4.46 ×10^8 cm^3/C respectively.

b- For $TlBiS_2$ single crystals

Measurements of the electrical conductivity and Hall coefficient are performed over the temperature range 153 K to 573 K. The energy gap is calculated to be ΔEg = 0.441eV. The crystal obtained have n-type conductivity with electron concentration of n= 1.654 ×10^{17} cm^{-3} at room temperature.

The electrical conductivity at room temperature equals to 0.0565 $(\Omega.cm)^{-1}$. The Hall mobility at 300K were evaluated as μ_H = 2.136 cm^2/V.sec the ionization energy of donor ΔE_d= 0.091 eV. and the Hall coefficient was found to be R_H= 37.78 cm^3/C.

2- Thermoelectric power (TEP) :

a-for $TlBiTe_2$ single crystals

The temperature dependence of the thermal e.m.f. in the temperature range extends from 219 K to 488 K was measured. The $TlBiTe_2$ sample appeared to be p-type. The electron and hole mobilities are found to be μ_n= 5.024×$10^3$$cm^2$/V.sec and μ_p = 2.258×10^3 cm^2/V.sec respectively. The effective masses of charge carriers are m_n^* = 1.82×10^{-29}Kg and m_p^* = 6.0933×10^{-27} Kg for electrons and holes, respectively.

The diffusion coefficient for both majority and minority carriers was estimated to be D_p= 58.4701 cm^2/sec and D_n = 130.1274 cm^2/sec respectively. The mean free time between collision can be deduced to be τ_p = 8.54×10^{-10} sec and τ_n= 5.68 ×10^{-14} sec for both holes and electrons. The diffusion length of holes and electrons are found to be L_p= 2.23×10^{-4} cm and L_n = 2.719 ×10^{-6} cm. In order to show the effectiveness of a material for thermoelectric applications. The dimensionless figure of merit was also determined and show the possibility of using this compound in thermoelectric generators.

b- For $TlBiS_2$ single crystals

Measurements of the thermoelectric power of a single crystal samples were carried out between 182.5 K to 505.5 K .This results indicated the n-type nature of the sample under investigation. The ratio of the electron and hole mobility is μ_n/μ_p= 9.87. The effective mass of holes is found to be m_p^*= 2.93×10^{-23}Kg. The obtained effective mass of electrons m_n^* = 2.75×10^{-31} Kg. The diffusion coefficient for both carriers holes and electrons was evaluated to be D_p= 0.0553 cm^2/sec and D_n= 0.5473 cm^2/sec respectively.

The mean free time between collision is estimated to be τ_p= 3.88×10^{-8} sec and τ_n= 3.607×10^{-15} sec for both holes and electrons respectively. The estimated diffusion length for holes and electrons is found to be L_p= 4.64×10^{-5}cm and L_n =4.44×10^{-8}cm. Also the figure of merit was calculation to be Z= 3.005×$10^{-10}$$k^{-1}$.

3- Switching effect investigations :

The switching phenomenon is one of the numerous interesting effects arising in strong electric field. This phenomenon has been observed in a great number of crystalline, a amorphous and liquid semiconductors. The discovery of this phenomenon attracts many researches because of its potential applications.
At present the nature of the switching phenomenon is not yet clear and the experimental data available have not been explained unambiguously. Conflicting explanation of the experimental data are due mainly to the complex nature of the switching phenomenon consisting of a series of independent stages during which different mechanisms can act. Throughout this work the results of switching effect for $TlBiTe_2$ and $TlBiS_2$ are presented .

a- For $TlBiTe_2$ single crystals

From the behavior of the switching phenomenon we can see that ;

* The process takes place with both polarities on the crystal and has symmetrical shape, and the switching parameters are sensitive to the temperature, light intensity and sample thickens as well.
* When the applied voltage exceeds a threshold voltage, the unit switching along the load line to the conducted state. The current control negative resistance type was noticed for the crystal under investigation.
* The memory switching effect in such crystal is an effect which appears after the negative resistance process.
* The parameters of the high- resistivity, low resistivity state depend to some extent on the quality of the sample and on the surrounding conditions. Investigation of the switching effect shows that the holding current increases as the temperature increases, while the holding voltage decreases with increasing the temperature.
* The VAC has S- shape type from the common form of the switching phenomena.

b- For $TlBiS_2$ single crystal

By investigation of the DC current-voltage characteristics of $TlBiS_2$ single crystal it has been found that;

* The specimen under test exhibit memory switching of the negative resistance process with the CCNR form.
* Memory state persists if the current is decreased slowly to its zero value. However, if current is forced to decay suddenly, the specimen returned to the high resistance state.
* The current – voltage characteristic is symmetrical with respect to the reverse of the applied voltage and current.
* The phenomenon in our sample is very sensitive to the temperature, intensity of white light, and sample thickness.
* The switching parameters (i_{th},V_{th},P_{th},i_h,V_h,R_{off}, R_{on}, E_{th}) are checked under the influence of different factors of the ambient conditions.

In view of these properties our best materials can be used in the field of switching elements and memory elements in electronic devices.
This mode of investigation (crystal growth and studying the transport properties in addition to switching phenomena) is the ideal way for finding out the possibility of making applications for these semiconductor compounds, especially in the field of energy conversion, devices, and electronic engineering.