

PbSnTe Single Crystal Growth and Studying Some Physical Properties.

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Abstract

Single crystal of PbSnTe compound was grown from melt by annealing furnace of two –zone. Some physical properties of prepared single crystal have been investigated experimentally. The crystalline structure of prepared ingot was determined by X-ray diffraction method. The source radiation was $\text{CuK}\alpha$ with wavelength $\lambda=1.54 \text{ \AA}$. The (XRD) observations shows that the single crystal structures with (224) plane. Thin ($16\mu\text{m}$) epitaxial PbSnTe films evaporated in a vacuum on the single crystal of (CaF_2) were investigated. The absorption spectra at the fundamental absorption edge of films have been measured at room temperature, which closed to the optical band gap in (0.13 eV) value. Measurements of current – voltage (I-V) of prepared films are exhibit linear behavior in the dark field.

الخلاصة

في هذا البحث نميت بلورة مركب (PbSnTe) من المنصهر النقي بأستخدام طريقة الفرن الحراري ذو النطاقيين. وقد تمت دراسة بعض الخصائص الفيزيائية للبلورة المفردة المنمأة. حدد التركيب البلوري للقلب المحضر بواسطة أنماط الأشعة السينية (XRD) مصدر الأشعاع المستخدم كان $\text{CuK}\alpha$ بطول موجي $\lambda=1.54 \text{ \AA}$. أظهرت فحوصات (XRD) أن اتجاه النمو البلوري هو بالمستوي (224). حضرت أغشية بسلك ($16\mu\text{m}$) وبطريقة الترسيب الفوقي على قواعد بلورية من شرائح (CaF_2). أن طيف الأمتصاص لحافة الأمتصاص الأساسية للأغشية المحضرة قد حدد وقيس بدرجة حرارة الغرفة وأظهرت الحسابات المستخلصة أن فجوة الطاقة البصرية تمتلك القيمة (0.13) إلكترون فولت. قياسات التيار – الفولتية للأغشية الرقيقة المحضرة تبين وجود خصائص خطية (اتصال أومي) في حالة الظلام.

Introduction

Narrow– gap IV-VI semiconductors of lead chalcogenide type at present are mostly applied to tunable diode laser devices for the (3-30) μm wave length range [Kinoshita and Yamada,1995]. Lead chalcogenide photovoltaic diode is high sensitivity and fast detectors for (1-3) μm , (2-5) μm and (8-14) μm windows as far as they are potentially related to optical bistability devices [Shani, *et al.*, 1985]. Lead chalcogenide semiconductor materials include the binaries PbS, PbSe and PbTe, and their solid solutions as eg. $\text{PbS}_{1-x}\text{Se}_x$ ($0 < x < 1$). Further ternary compounds contain Sn as eg. $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ ($0 < x < 1$) or $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$ ($0 < x < 0.4$). All these compounds crystallize in the cubic rock salt structure and are characterized by a direct gap located at the L point of the Brillion zone. Surfaces of constant energy are prelate ellipsoids with the long axes in the four equivalents (111) - direction. The anisotropy ratio is roughly 1.3 for PbS, 1.9 for PbSe and 8 for PbTe in both conduction and valence band with only slightly different effective masses in both bands [Preier, 1979]. The gap becomes zero in $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ for $x = 0.4$ and in $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$ for $x = 0.2$. At higher x values the lowest conduction and the highest valence band become inverted.

Lead chalcogenides exhibit a gap turing rate of $dE_g / dT = +4\text{cm}^{-1}\text{K}^{-1}$, below 60K, turing decreases gradually [Fripp, *et al.*, 1985]. In lead chalcogenide samples

free carriers concentrations are rarely below 10^{17} cm^{-3} [Shani, *et al.*, 1985]. At $\lambda=10 \mu\text{m}$ for $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$ with $E_g = 120 \text{ meV}$, the absorption coefficient = 20 cm^{-1} at room temperature, and 2 cm^{-1} at cryogenic temperatures. Lead chalcogenides exhibits poor heat conductivity [Melngailis and Harman, 1968].

Experimental Technique:

Until the early 1950s, the development of infrared opto-electronics devices revolved principally around polycrystalline films of lead chalcogenide. The success of semiconductor physics based on single crystal techniques develops the performance of opto-electronics devices. In this study PbSnTe single crystal was prepared by annealing furnace of two- zone as following manner, and the setup is schematically shown in Fig.(1).

A - Quartz Ampoule Preparation:

A long quartz ampoule ($L = 15 \text{ cm}$ and inner diameter $\phi = 10 \text{ mm}$) was carefully cleaned using laboratory detergent and cleaner solution, wiped with soft cloth, and then washed with tap water. Then the ampoule was rinsed by ultrasonic bath filled with isopropyl alcohol for about (15 minutes). Finally the ampoule was rinsed by H_2F acid for (5 minutes) washed ionized water, and backed. Astoichiometric mixture of ternary compound contain Sn as $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ ($0 < x < 1$) of high purity was taken in a quartz tube which was vacuum sealed off at pressure of 10^{-5} mbar . The liquid nitrogen was used to increase the vacuum efficient.

B – Crystal Growing and Furnace Control:

The crystal growth operation was done by using furnace of cylindrical chambers was developed as controller and tester electronic circuits. The annealing range of two – zone furnace (temperature raising and lowering) with ampoule distance in the zone was selected, and the protection cover was used inside the furnace to provide the explosion influence of ampoule.

A quartz ampoule is located in a two – zone furnace with the central axis for heating quality. The sealed ampoule was heated to temperature (900°C) slowly (above 30°C of melting point of compound), and maintained at the temperature of (870°C) for (48 hrs). Then the furnace temperature was slowly reduced as ($1\text{-}3^\circ\text{C/hr.}$) to (500°C), and cooled to room temperature as shown in Fig.(2).

Experimental Measurements:

The sealed ampoule was taken out the furnace, and directly broken. The crystal ingot was formed as the ampoules dimension Fig.(3). Philips X-rays diffractometer was used to determine the crystalline structure of the PbSnTe ingot. FTIR spectrophotometer from Perkin Elemer was used to carry out the absorption spectrum in the ($2\text{-}16 \mu\text{m}$) region for the prepared PbSnTe thin films. These films were prepared using molybdenum boat to sublime PbSnTe powder on CaF_2 crystal slide in a vacuum of order (10^{-5} mbar). Synthetic PbSnTe was vacuum – sublimed at a rate of (1.3 nm/sec.) and films substrate was heated to (250°C) for epitaxial growing.

The films were deposited on windows of CaF_2 crystals with transmission about (83%). The absorption coefficient was calculated using the following equation [Pankove, 1971]:

$$\alpha = 2.3 \frac{A}{t} \dots\dots\dots(1)$$

Where t is the thickness and A is the absorbance given by:

$$A = \log_{10} \frac{I_0}{I} = \log \frac{100}{T} \dots\dots\dots(2)$$

Where I_0 is the incident light and T is the percentage transmittance. The extinction coefficient was calculated by using the following formula [Pankove, 1971]:

$$k = \frac{\alpha\lambda}{4\pi} \dots\dots\dots(3)$$

The current – voltage (I-V) characteristics in the dark field were recorded using a D.C. variable – voltage power supply, and digital multimeter (hp-3465A) at 273 K temperature.

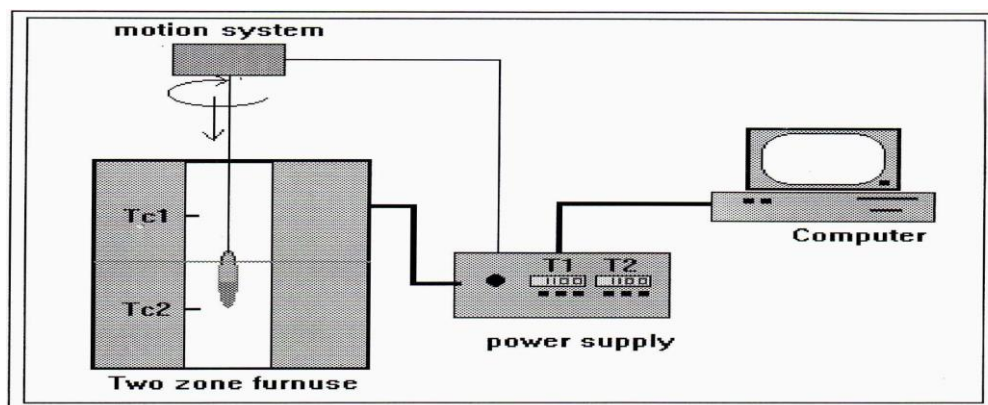


Fig. (1) Crystal growth system (vertical).

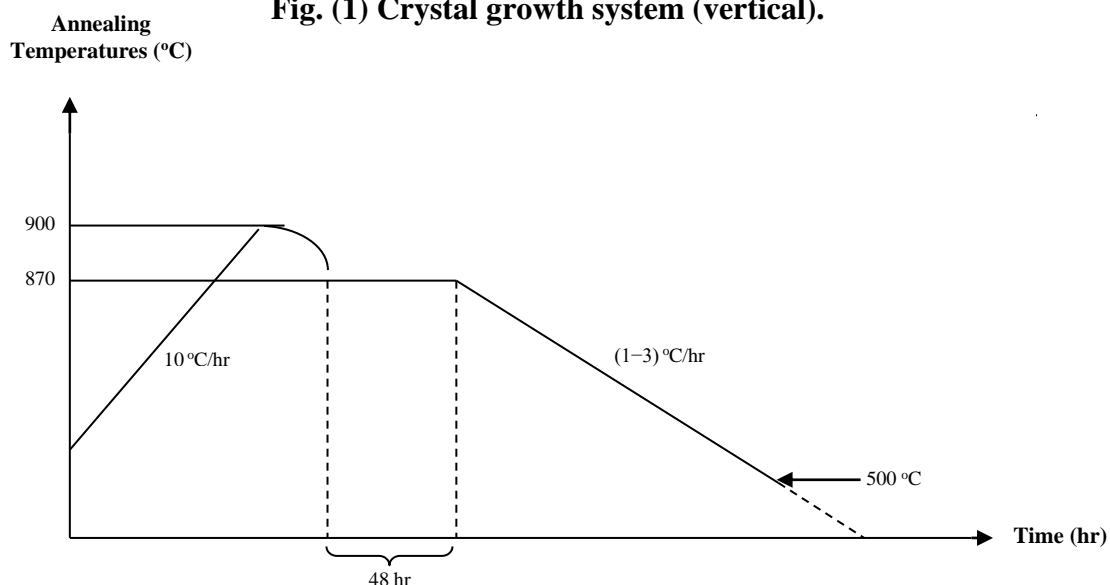


Fig. (2) Diagram of temperature variation for furnace with annealing time.



Fig. (3) Prepared PbSnTe ingot of 10 gm.

Results and Conclusions

The main characteristics of PbSnTe crystal grown from pure melt have been revealed by an analysis of its X-ray diffraction patterns, absorption edge of absorption spectrum and (I-V) characteristics.

The X-ray diffraction analysis of crystal ingot wafer which prepared as crystallization axis and fine polishing, indicates that the crystal grown in (224) direction and appears a single peak of high intensity as shown in Fig.(4). These observations were corresponded to patterns of PbTe single crystal Fig.(5).

In the case of PbSnTe powder, the (XRD) patterns Fig.(6) shows there is no an expected growth peaks which appears. From the d-spacing calculating and corresponding to ASTM card of PbTe compound, and (XRD) of its powder Fig.(7), we found a good agreement in both values. The peak deviation was attributed to molarities percentage of Sn in PbSnTe compound system.

The absorbance spectrum of PbSnTe thin films in the spectral range (2-14) μm as shown in Fig.(8). The absorption and extinction coefficients were measured and the plot of $(\alpha h\nu)^2$ against $(h\nu)$ is shown in Fig.(9). The values of optical energy gap are closed to (0.13 eV). Similar results were obtained by Johnson [Johnson and Parker 1981]. The increase in absorption coefficient in the range of (8-14) μm is clear and takes higher values ($>10\text{cm}^{-1}$), which results from the electronic transitions of valence band and the impurities and the transitions of energy bands. The dependence of the extinction coefficient (k) obtained by using equation (3) on wavelength is shown in Fig.(10). The behavior of (k) is similar to the corresponding absorption coefficient Fig.(11).

(I-V) measurements were made for PbSnTe thin films showed that, the (I-V) characteristics in the dark field were linear in the voltage range (0.05-2 Volt). This indication due to thin films made ohmic contacts with vacuum- deposited aluminum electrodes as shown in Fig.(12).

Finally, we note that the single crystal ingot prepared from pure melt by using the annealing of two- zone furnace are primarily succeeded and distinguished from (XRD) patterns study and some physical properties. We believed that our results are in agreement with other previous studies [Runyan, Johnson *et al.*, Kinoshita, Yamada and Ito *et al.*, 1975, 1981, 1995 and 1999]. The availability of single crystal ingot for PbSnTe devices has already made its impact in infrared instrumentation and a number of applications [Harman, Hurst, Ferreira *et al.*, Mohammed, Gate *et al.* and Shklover *et al.* 1973, 1990, 1999, 2002, 2002, 2003 and 2005].

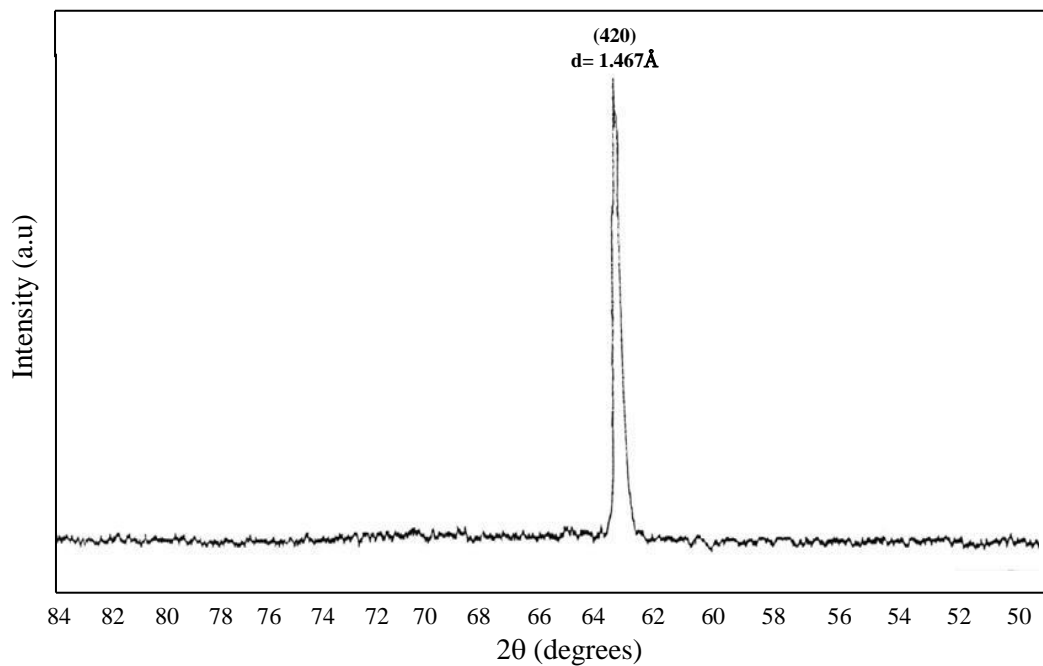


Fig.(4) The X-ray diffraction patterns of PbSnTe single crystal sample.

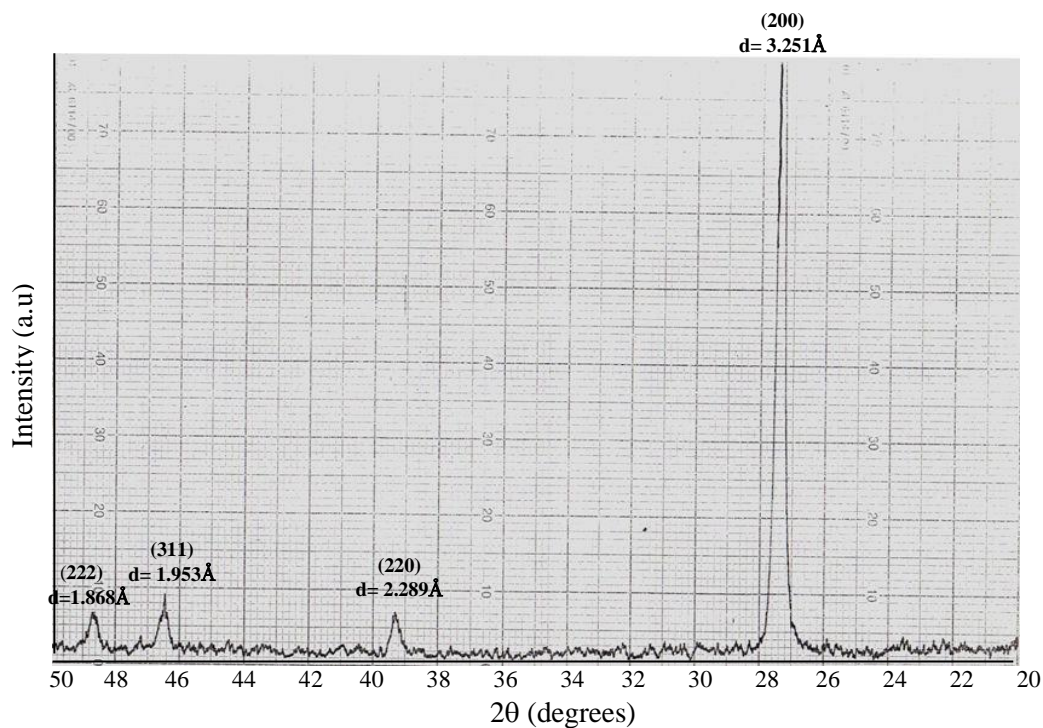


Fig. (5) The X-ray diffraction patterns of PbTe single crystal.

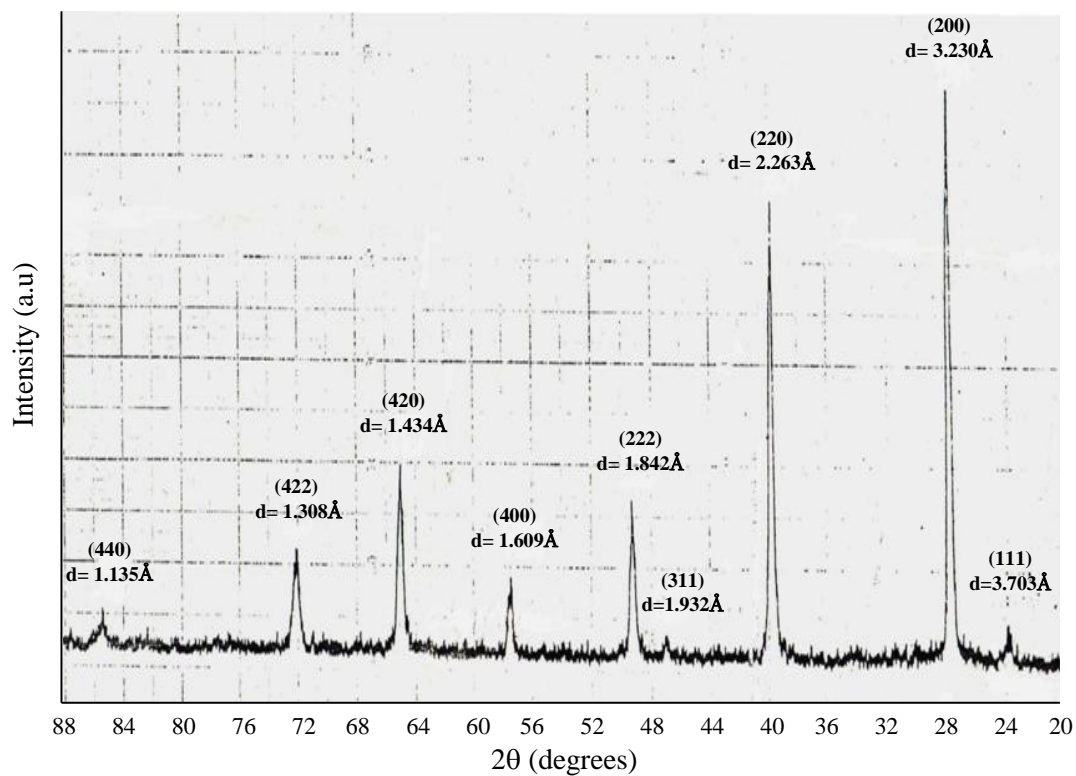


Fig. (6) X-ray diffraction of PbSnTe powder.

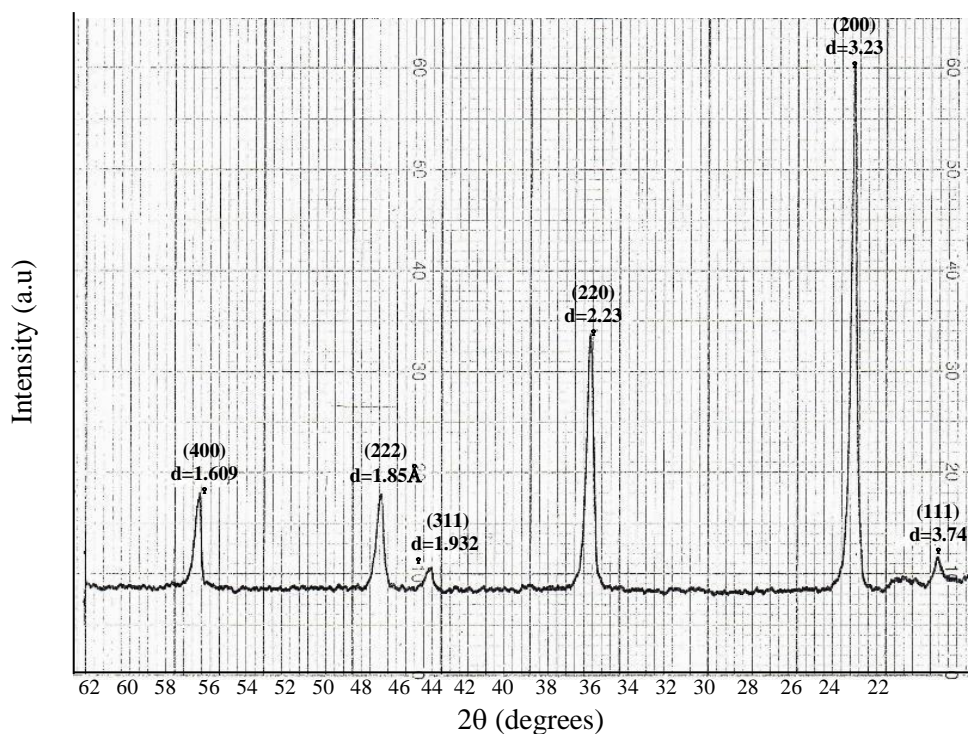


Fig. (7) The X-ray diffraction patterns of PbTe powder.

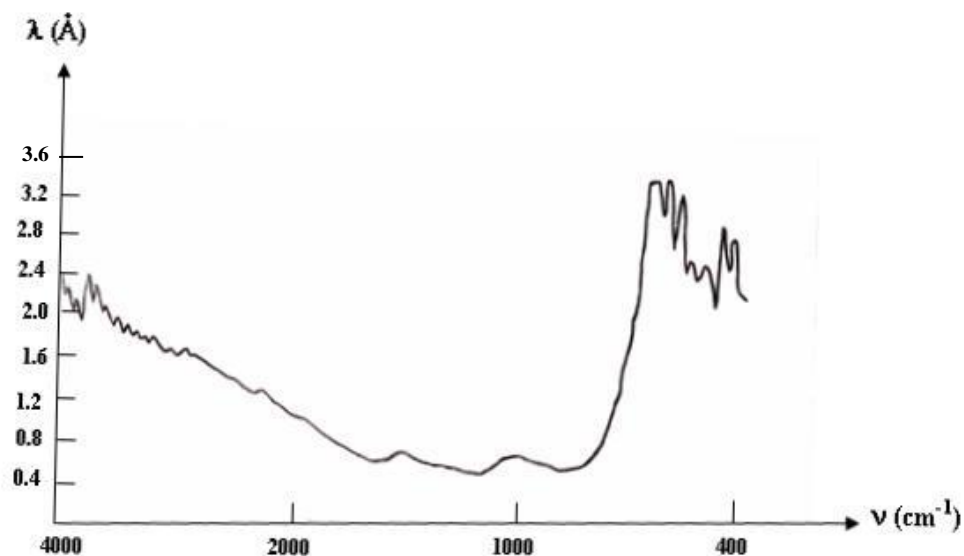


Fig.(8) The absorbance spectrum of PbSnTe films at room temperature.

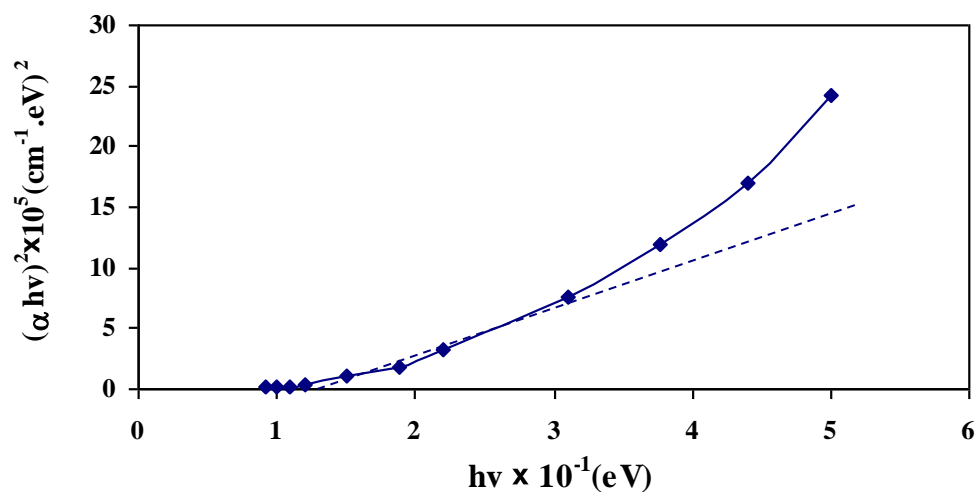


Fig. (9) $(\alpha hv)^2$ as a function of photon energy ($h\nu$) for PbSnTe films at room temperature.

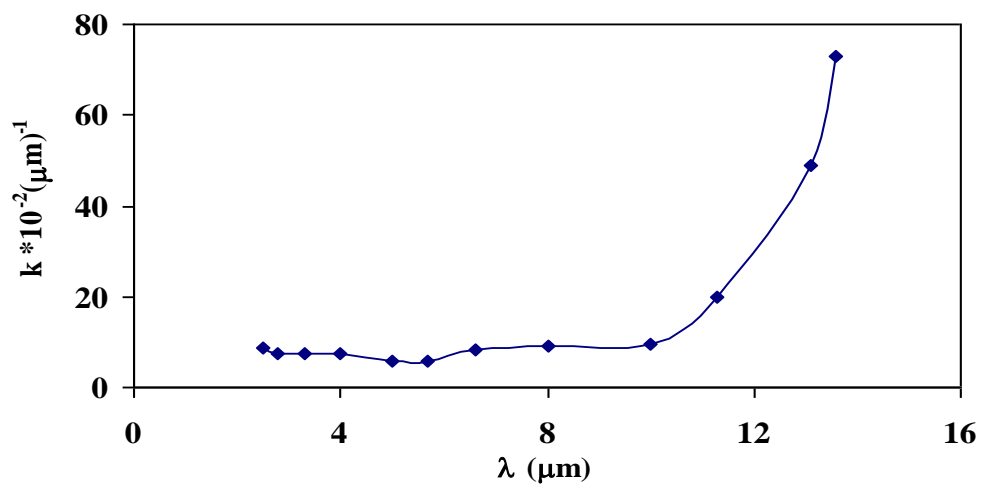


Fig. (10) Variation of extinction coefficient with wavelength for PbSnTe films at room temperature.

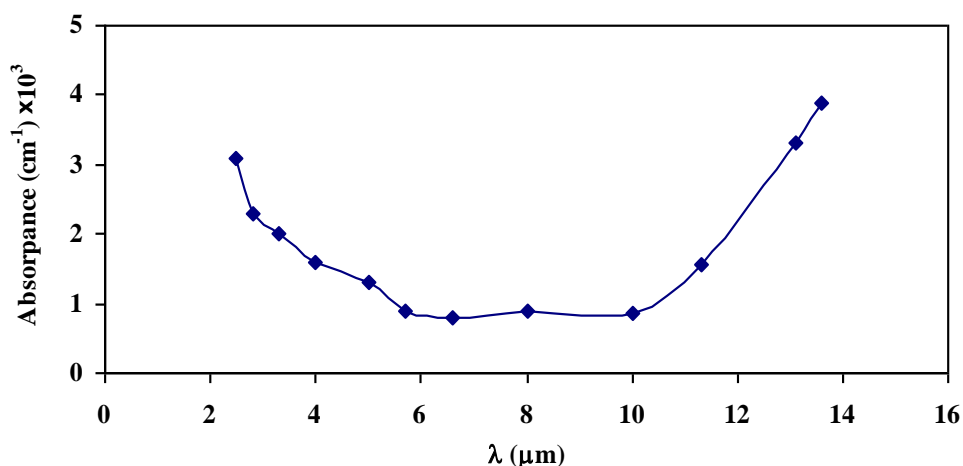


Fig.(11) The absorption spectra of PbSnTe film.

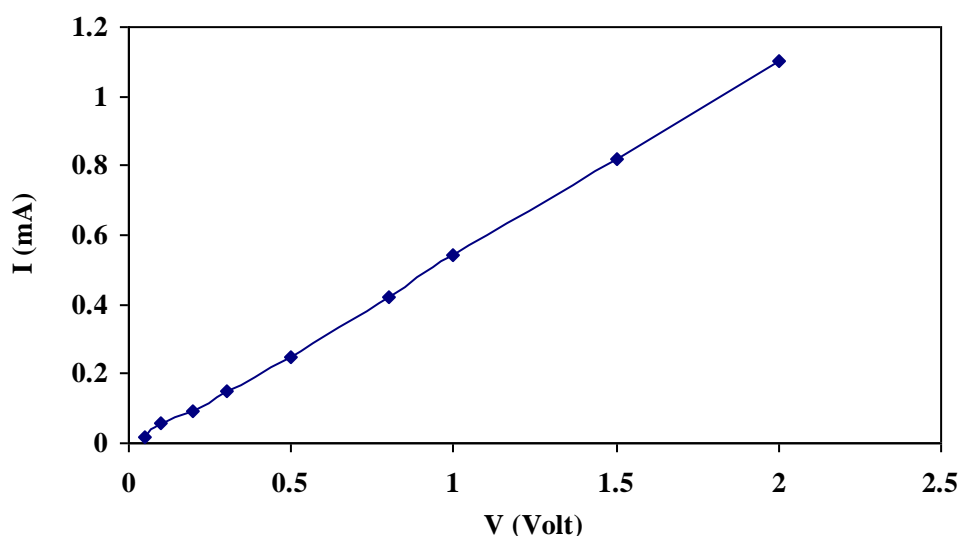


Fig.(12) I-V characteristics for PbSnTe thin films at room temperature.

References

- Ferreira S.O., Rappl P.H.O, Closs H., Abramof E., Motisuke P., Ueto A.Y., and Bandeira I.N., 1999, " Band Crossing Evidence in PbSnTe Observed by Optical Transmission Measurements", Brazilian Journal of Physics, Vol.29, No.4, pp.771-774.
- Fripp A.L., Crouch R.K., Debnam W.J., Clark I.O., and Wanger J.B., 1985," Effect of supercooling in the initial solidification of PbTe-SnTe solid solutions", J. Crystal Growth, Vol.73 , p.304.
- Gates B., Lu Y., Li Z., Xia Y., 2003, "Fabrication and characterization of photonic crystals with well- controlled thickness and stop band –attenuation," Appl. Phys A., Vol.76 ,, p.p 509-513.
- Harman T.C., 1973," Control and Imperfections in Crystal of PbSnTe, PbSnSe and PbSSe " J.Nonmetals , Vol.1, p.183.
- Hurst J.H., 1990,"Electrochemical visualization of convection in liquid metals" Ph.D.Dissertation, the university of Florida, chemical engineering.
- Ito M., Seo W.S. and Koumoto K., 1999," Thermoelectric Properties of PbTe Thin

- Films Prepared By Gas Evaporation Method "(J. Mater. Res), Vol. 14, No.1, p. 209.
- Johnson R.W. and Parker S.G., 1981" Preparation and properties of PbSnTe " in preparation and properties of solid state materials, Ed.W.R.Wilcox, Marcel Dekker,Inc.,New York , Vol.6 , p.1.
- Kinoshita K. and Yamada T., 1995 "Pb_{1-x}Sn_xTe Crystal Growth in Space", J. Crystal Growth, Vol.147, pp.91-98.
- Melngailis I. and Harman T.C., 1968, "Photoconductivity in single-crystal Pb_{1-x}Sn_xTe" Vol. 13 , No.5 ,PP.345-351.
- Mohammed G. H., 2002, "Optoelectronic Parameters of Pb_xS_{1-x} Thin Films" M.Sc. Thesis, Baghdad Univ. Coll. Scie. Physics Dep.
- Pankove, J.I., 1971," Optical Processes in Semiconductors", London.
- Preier H., 1979, "J. Appl. Phys", Vol.20, No.189.
- Runyan, W.R., 1975,"Semiconductor Measurements and Instrumentation", McGraw-Hill, (Tokyo: Kogakuth Ltd.).
- Shani Y., Rosman R., Katzir A., 1985, "Calculation of the refractive indexes of lead chalcogenide salts and its application for injection lasers" Vol.21 , No.1,pp.51-62.
- Shklover V. ,Hofman H., Braginsky L. , 2005 , " Domain structure and optical properties of thin nanocrystalline arrays ," in enabling photonic technologies for defense, security , and aerospace applications , A.R.Pirich, M.J.Hayduk, E.J.Donkor , P.J.Delfyett, Jr.eds,proc.SPIE 5814, pp.239-247.