

## Crystal Growth of High – Purity $\text{Bi}_2\text{Se}_3$ and Study of Crystal Structure

†A.H.Abd-Al Kathum Al Mohanna, †U.A.Khalid and \*Ghuson H.Mohammed

†University of Basrah , Collage of Science, Physics Department

\*University of Bagdad , Collage of Science, Physics Department,

E-mail :Ghuson \_hamed @Yahoo.com

### Abstract

The  $\text{Bi}_2\text{Se}_3$  compound was synthesis by fusing initial compounds consisting of extra pure elements in stoichiometric ratio from elements compound, charged inside quartz ampoule. The crystal growth of  $\text{Bi}_2\text{Se}_3$  carried out using Brighaman technique process from melting f (Bi+Se ) at temperature of 810 °C for about 48 hrs. Single crystal of  $\text{Bi}_2\text{Se}_3$  has been grown in direction (211) after slow cooling on account of heat gradient to zone furnaces at cooling rate (1-3) C/hr. The structure study of the compound was determined by x-ray diffraction technique, which it has bismuthinite structure and orthorhombic unit cell with lattice parameters of  $a=10.2678 \text{ \AA}$ ,  $b=11.2392 \text{ \AA}$  and  $c=5.1737 \text{ \AA}$

أنماء بلورة  $\text{Bi}_2\text{Se}_3$  عالية النقاوة ودراسة خصائصها  
ارشد حمود عبدالكاظم واسامة عبدالله خالد وغصون حميد محمد

### الخلاصة

حضر المركب  $\text{Bi}_2\text{Se}_3$  بواسطة صهر عناصره الاولية عالية النقاوة بنسب وزنية مكافئة لتكوين المركب ، داخل امبولة من الكوارتز. نميت بلورة مفردة من المركب بتقنية برجمان من صهر العناصر (Se+Bi) بدرجة حرارة  $810^\circ\text{C}$  لمدة 48hr. درس التركيب البلوري لبلورة المركب  $\text{Bi}_2\text{Se}_3$  المفردة باستخدام تقنية حيود الاشعة السينية ظهر نمو بلوري عالي الشدة (211) باتجاه كما درس التركيب البلوري لمسحوق المركب بتقنية حيود الاشعة السينية ووجد انه يمتلك تركيب بلوري البزموثينايت ذات وحدة خلية معيني قائم ذات ابعاد  $a= 10.2678 \text{ \AA}$ ,  $b=11.2392 \text{ \AA}$ ,  $c= 5.1737 \text{ \AA}$

### Introduction

Recently a considerably increasing interest has been observed in using binary semiconducting chalcogenides with the formula group  $\text{V}_2\text{-VI}_3$  compound as photoconductors materials <sup>(1,2)</sup>. Many  $\text{V}_2\text{-VI}_3$  compounds super lattice and multilayer with different structure have studied experimentally <sup>(3,4)</sup>, and some characteristics of these compounds . In these system, the energy band barriers for med by wide gap materials are  $\text{As}_2\text{S}_3$  ,  $\text{As}_2\text{Se}_3$ ,  $\text{Sb}_2\text{S}_3$  until  $\text{Bi}_2\text{Se}_3$  <sup>(5)</sup>, also have narrow – band gap material which forms  $\text{Sb}_2\text{Se}_3$  ,  $\text{Sb}_2\text{Te}_3$  and

$\text{Bi}_2\text{Te}_3$ . These compounds have orpiment structure contain the arsenic element as stoichiometric ratio such as  $\text{As}_2\text{S}_3$  that has monoclinic unit cell <sup>(6)</sup> either stibnite which contains antimony element at stoichiometric in crystal structure as  $\text{Sb}_2\text{S}_3$  or bismuthinite structure which contains bismuth element in stoichiometric ratio as  $\text{Bi}_2\text{S}_3$  and  $\text{Bi}_2\text{Se}_3$  , also it has orthorhombic unit cell and have space group  $(\text{pnma} - D_{16}^{2h})$  <sup>(7,8)</sup>. Several workers study the compounds  $\text{V}_2\text{-VI}_3$  group and found that the dimension of lattice parameters are  $a=4.134 \text{ \AA}$  and  $c=28.611 \text{ \AA}$   $\text{Bi}_2\text{Se}_3$  <sup>(9)</sup>. These

compounds have some unique properties that are different from other compounds, these are direct wide energy gap, structure variation with force field, that leads to the variation of carriers concentration and mobility. These properties made these compounds of great interest in electronic application that contests the other groups of semiconductors.

### Experimental Procedure

The  $\text{Bi}_2\text{Se}_3$  compounds was synthesis by fusing initial compounds consisting of extra pure elements (Bi:99.999% from Balzers com.) and (Se : 99.999% from Aldrech com.) in stoichiometric from elements compound placed inside quartz ampoule after sealed on side to work tip. The quartz ampoule was evacuated to  $10^{-6}$  torr, the ampoule with its charge was placed in a single zone, tube furnace type Lindbergh. The was heated above the melting point of the compound to  $810^\circ\text{C}$  at range  $1.5^\circ\text{C}/\text{min.}$  The ampoule was kept for 48 hr. in the zone furnace at that temperature. The melt was shaken during heating several times then cooled slowly at range of  $(1-3)^\circ\text{C}/\text{hr.}$  on gradient heat inside zone furnace and along the solidification direction to axis furnace in Fig.(1). After solidification process for melt at low temperature we obtain single crystal from  $\text{Bi}_2\text{Se}_3$  take container shape which consisted as show in Fig.(2).

X-ray diffraction analysis contain that  $\text{Bi}_2\text{Se}_3$  in single crystal, powder and thin films. After evaporation compound in vacuum  $10^{-5}$  torr on clean glass microscopy substrate at room temperature by thermal evaporation method. The thickness of the deposited films was  $0.664\ \mu\text{m.}$

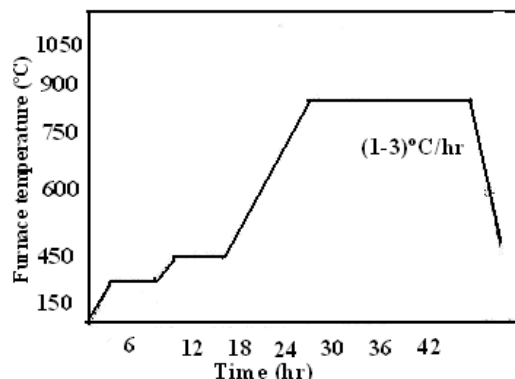


Fig.(1) Thermal diagram of various furnace temperature and heating time.

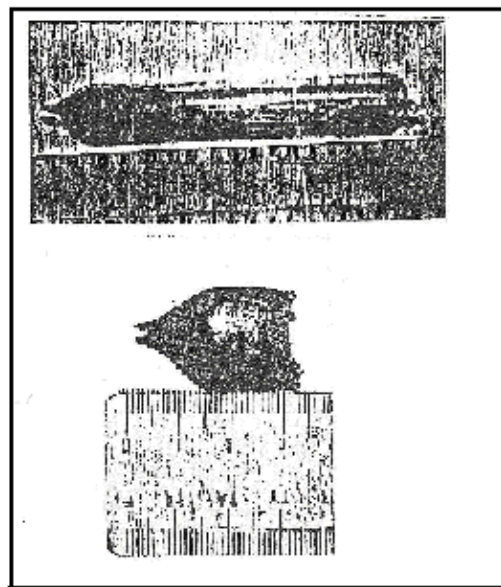


Fig. (2) Grown  $\text{Bi}_2\text{Se}_3$  Single crystal by slow cooling method

### Result and discussion

The result to crystallographic studies of  $\text{Bi}_2\text{Se}_3$  powder at room temperature is shown Fig. (3). It is clear from the x-ray diffraction pattern that the compound has a bismuthinite structure of orthorhombic unit cell with lattice parameters  $a=10.2678\ \text{\AA}$ ,  $b=11.2392\ \text{\AA}$  and  $c=5.1737\ \text{\AA}$ . From these results the direction (211) is preferable which have high intensity percent comparing with other peaks. Also the x-ray diffraction

pattern of single crystal of  $\text{Bi}_2\text{Se}_3$  revealed that growth is (211) direction after perpendicular cutting of crystal axis (9, 10)

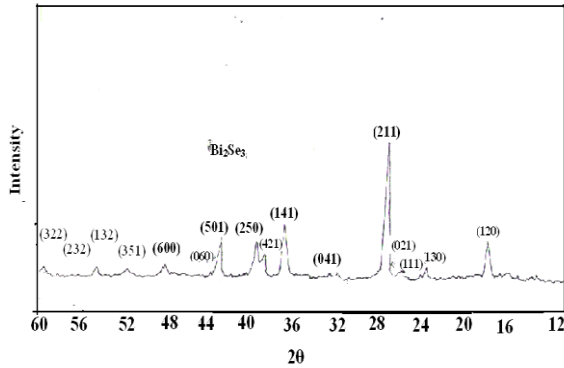


Fig. (3) XRD patterns for powder of  $\text{Bi}_2\text{Se}_3$ .

This direction shows preferred orientation as shown Fig. (4). But there are few surface defects result from cutting and polishing processes. To get ride of many processes were performed such as long period of polishing, ultrasonic cutting, and crystal surface etching.

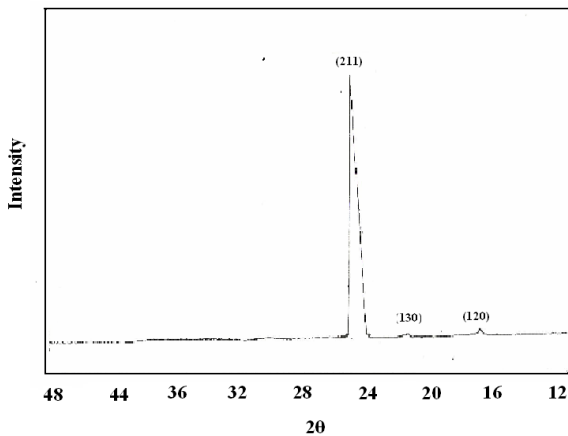


Fig.(4)XRD patterns recorded using Cuka radiation for single crystal.

Thin films to  $\text{Bi}_2\text{Se}_3$  have amorphous structure but after heat treatment small peaks appear which an indication polycrystalline structure to the films at temperature 250 °C for one hour and this polycrystalline structure is due to grain

size growth <sup>(11)</sup> in Fig.(5). The fusion of grains with nearest neighbors from islands that have preferred orientation in (250) direction for the most thin films with annealing at temperature 250 °C.

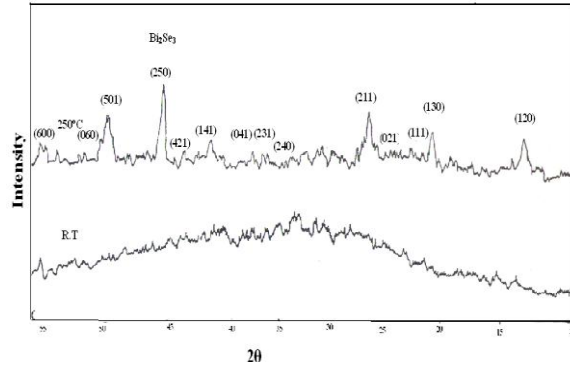


Fig. (3) XRD patterns for thin films at R.T and annealing at 250°C for 1 hr. of  $\text{Bi}_2\text{Se}_3$ .

### Conclusion

The compound  $\text{Bi}_2\text{Se}_3$  prepared from high purity (99.999%) ordinary element with stoichiometric ratio by reaction fusion inside evacuated ampoule. X-ray diffraction pattern study shows that the compound  $\text{Bi}_2\text{Se}_3$  have polycrystalline bismuthinite structure. The single crystal growth by brighman technique of compound.

### Reference

- [1] 1-H. Hu, O. Gomez-Daza and P. K. Nair, J.Mater. Res.,13, 2453(1998).
- [2] 2-S. Ourai, M. Taniyama, S. Kryomoto, T.Makino and K.Matsui, phys.Stat.Sol.b,211,263(1999).
- [3] 3- I. K. El-Zawawi, A. A. El-Moez, F. S. Terra and M. Mounir, FIZIKAA, 3, 97(1998).
- [4] 4-P. pramanik, R.N. Bhattacharya and A.Mondel, Electronchem.Soc., 127, 1857(1980).
- [5] 5-B. Roy, B. R. Chakraborty, R. Bhattacharya and A. K. Dutta, SolidState Commun.,25,937(1978).
- [6] 6-N. V. Belov, Yu. G. Zagalshkaya and E. A. pobedimskaya,

- Dokl.Akad.Nauk.SSSR,209,1330 (1973).
- [7] 7-P. Arun and A.G. Vedeshwar, J.Mater. Sci.b,31,7570(1996).
- [8] 8-L. Cervinka and A.Flruby,J.Non-Crystalline Solid, 48,231(1982).
- [9] 9-R. Novotny, P. Lostak, L.Benes and J. Horak, Crystal Growth,69, 301(1984).
- [10] 10- Hassan. J. G.,N. A. Abd Al Hasien, W. A. Taha, Crystal growth and thin films preparation for quaternary compound  $ZnGe_{0.5}Si_{0.5}As_2$  and study some physical proporation, Thesis M.Sc. University Basrah, (2001).
- [11] 11- A. H. Abd Al Kathum, K. S. Majdi, W. A. Taha, Crystal growth and thin films preparation of the compounds  $Bi_2Se_3, Sb_2S_3$  and the mixture  $Bi_2(1-x)Sb_2xS_3$  and study structural, optical and electrical properties, Thesis M. Sc. University Basrah (2001).