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Research paper

Melting point and microhardness of Cu_2-II-IV-VI_4 compounds

Salah Daoud[1]*, Hamza Rekab-Djabri[2,3], Nabil Beloufa[2]

[1] *Laboratory of Materials and Electronic Systems (LMSE), Bordj Bou Arreridj University, 34000 Bordj Bou Arreridj, Algeria*
[2] *Laboratory of Micro and Nanophysics (LaMiN), Oran ENP, BP 1523, El M'Naouer, 31000, Oran, Algeria*
[3] *Faculty of Nature and Life Sciences and Earth Sciences, Akli Mohand-Oulhadj University, 10000, Bouira, Algeria*
**Corresponding author E-mail:salah_daoud07@yahoo.fr*

Abstract

In the present study, we investigate the correlation between the melting point Tm and the microhardness H of some tetragonal and orthorhombic Cu_2-II-IV-VI_4 semiconducting compounds. After analyzing the experimental data of both Tm and H, we found that the melting point Tm of Cu_2-II-IV-VI_4 compounds correlates linearly with the microhardness H. With a coefficient of the correlation of around 0.98, the best fit was obtained using the linear model as follow: T_m = 175.54 H +792.27. The significance of the regression is given as the probability P of the null hypothesis (that there is no correlation) $P < 0.0001$, while the average error on the estimation of the melting point Tm was found only at around 1.54%. Our expression related Tm and H was used to predict the microhardness H of Cu_2ZnSnS_4 (CZTS) material. Our value (2.68 GPa) of H of CZTS deviates from the theoretical one (2.7 GPa) by only around 0.74%.

Keywords: *Cu_2-II-IV-VI_4 Semiconductors; Melting Point; Microhardness; Linear Correlation.*

1. Introduction

Cu_2−II−IV−VI_4 semiconducting materials have been of great interest for many years because of their appearance as naturally occurring minerals and suitable band-gap energies for applications in various solar energy converters [1]. Using X-ray diffraction (XRD) patterns, field emission scanning electron microscope (FE-SEM), and Raman spectroscopy (RS) techniques, Khalateet al.[2] have investigated the effect of deposition temperature on the morphology as well as the physical properties of Cu_2ZnSnS_4 thin films deposited by spray pyrolysis technique at different substrate temperature. They found that all the CZTS films exhibited kesterite structure without any secondary phases, possessing band gaps lie between 1.49 and 1.57 eV.

Using first-principles approach, Gürel and co-authors [3] studied the structural, elastic, and dynamical properties of both Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ in kesterite and stannite structures. They mentioned that no significant difference between the calculated energetic, mechanical, and dynamical properties of the kesterite and stannite phases of either compound was observed.

Gujaret al.[4] have studied the synthesis of Cu_2ZnSnS_4 (CZTS) films by pulsed laser deposition (PLD) and effect of sulfur annealing on structure, composition, morphological and optical characterization of CZTS thin films using Raman spectroscopy (RS) techniques, scanning electron microscope (SEM), and Ultraviolet–visible (UV–Vis) spectroscopy. They found that all the CZTS films exhibited kesterite structure, possessing band gaps lie between 1.60 and 1.40 eV.

Many works [5-12] mentioned that several thermal and mechanical properties are strongly correlated in the semiconductors. Matsushita et al.[13] found that the melting point T_m correlates linearly to the mean atomic weight M for Cu_2-II-IV-VI_4 compounds, while Adachi [1] mentioned that the shame tendency between T_m and the effective cubic lattice constant a_{eff} was observed.

In the present work, we investigate the correlation between the melting point T_m and the microhardness H of some tetragonal and orthorhombic Cu_2-II-IV-VI_4 (II = Zn, Cd, Hg; IV = Si, Ge, Sn) semiconducting compounds. In addition the microhardness H of Cu_2ZnSnS_4 (CZTS) compound was obtained and analyzed.

2. Theory, results and discussion

We compile in Table 1 the melting points T_m and the microhardness H reported for a number of Cu_2-II-IV-VI_4 semiconductors [1].

Table 1: Melting Point T_m, and Microhardness H of Some Cu_2-II-IV-VI_4 (II = Zn, Cd, Hg; IV = Si, Ge, Sn) Semiconducting Compounds [1]

Materials	Structure-type	T_m (K)	H (GPa)
Cu_2ZnSiS_4	Orthorhombic	1396	3.4
$Cu_2ZnSiSe_4$	Orthorhombic	1246	2.8
Cu_2ZnGeS_4	Tetragonal	1377	3.4

Cu_2CdSiS_4	Orthorhombic	1289	2.5
$Cu_2CdGeSe_4$	Tetragonal	1107	1.9
Cu_2CdSnS_4	Tetragonal	1190	2.2
$Cu_2CdSnSe_4$	Tetragonal	1054	1.5
$Cu_2HgSnSe_4$	Tetragonal	1032	1.4

The different data of the experimental melting point T_m and microhardness H of some Cu_2-II-IV-VI_4 semiconducting compoundssummarized in Table 1are plotted in Figure 1. We can observe clearly that the melting point T_m increases linearly with increase of the microhardness H. The best linear fit was given as follows:

$$T_m = 175.54\ H + 792.27 \quad (1)$$

Where T_m is expressed in K, and H in GPa.
The significance of the regression is given as the probability P of the null hypothesis (that there is no correlation) $P < 0.0001$, while the average error on the estimation of the melting point T_m was found only at around 1.54%.

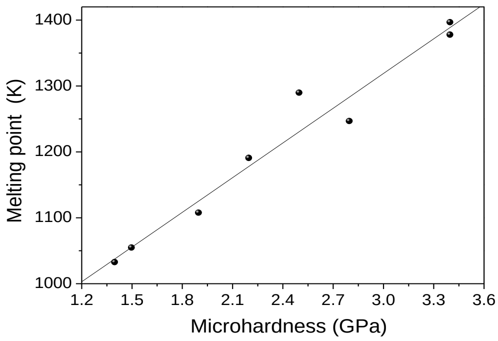

Fig. 1: Melting Point T_m versus the Microhardness H of Some Cu_2-II-IV-VI_4 Semiconducting Compounds.

Reciprocally, our expression related T_m and H can be used to predict the microhardness H of other Cu_2-II-IV-VI_4 semiconducting compounds.Our expression related T_m and H was used to predict the microhardness H of Cu_2ZnSnS_4 (CZTS) material. Replacing T_m = 1263 K of CZTS reported by Matsushita et al. [13] in Eq. (1), the value of H of CZTS was found equal to 2.68 GPa, which deviates from the theoretical one (2.7 GPa) [1] by only around 0.74%

3. Conclusion

Based on the experimental data reported in the literature, we investigate the correlation between the melting point $T_m$andthe microhardness H of Cu_2-II-IV-VI_4 semiconducting compounds. We found that the melting point T_m increases linearly with increase of microhardness H, as follow: $T_m = 175.54\ H + 792.27$, where T_m is expressed in K, and H in GPa.
Reciprocally, our expression related T_m and H was used to predict the microhardness H of CZTS material. Our value of H (2.68 GPa) deviates from the theoretical one (2.7 GPa) by only around 0.74%.

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