Int J Thermophys (2010) 31:1186–1194
DOI 10.1007/s10765-010-0787-8

Lattice Thermal Expansion and Ionicity for III_2–VI_3 Binary Defect Tetrahedral Compound Semiconductors and Their Alloys

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Received: 27 May 2009 / Accepted: 5 July 2010 / Published online: 20 July 2010
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Abstract A model for calculating the lattice thermal expansion is modified to be applicable to binary defect tetrahedral compounds that belong to the III_2–VI_3 group. The number of valence electrons for the expected missing atom as a vacancy is used to correlate the deviations caused by the ionicity of this group of compounds. The ionicity effects which are due to the different numbers between vacancy atom types, which in this case is the group III element, and the element itself, were also added to the correlation equation. In general, the lattice thermal expansion for a compound semiconductor can be calculated from a relation containing the melting point, the mean atomic distance, and the number of valence electrons for the atoms forming the compound. For compounds that undergo a structural change during heating, the phase transition temperature has the same role as the melting point for calculating the lattice thermal expansion that belongs to the related structure phase. The value of the mean ionicity for this group of compounds is also calculated and found to be equal to 0.416.

Keywords Defect tetrahedral compound · Ionicity · Phase transitions · Thermal expansion · III_2–VI_3 semiconductors

1 Introduction

Compounds of the III_2–VI_3 group with a defect zinc-blend structure occupy, with respect of their chemical composition, an intermediate position in the isoelectronic series of the diamond group between III–V and II–VI compounds. However, almost all properties of III_2–VI_3 group compounds, except for the forbidden bandwidth and micro-hardness, do not have values intermediate between the corresponding values for

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neighboring non-defect compounds in a given isoelectronic series, that is, in a series of substances having the same number of inner electrons [1,2].

The bulk of the binary compounds of III_2–VI_3 type received some attention in the mid-twentieth century [3,4]. The interest for this binary group compounds has been renewed in the last few years in two respects: first, they, under particular growth conditions [5], may form as II–VI/III–V interfaces and modify the electronic properties of junctions such as in optoelectronics, radiation detectors, and electrical switching applications [6,7] and second, they have been successfully prepared in bulk [8,9] as well as nanoscale size crystals, nanowires, and thin films [10–13].

In this work, attempts will be made to extend the model for calculating the lattice thermal expansion originally modified by Omar [14,15] for normal tetrahedral compound semiconductors to be applicable for the binary defect tetrahedral compounds group III_2–VI_3 and their alloys.

2 Methods of Calculation and Analysis

It is well known that the lattice thermal expansion α_L for tetrahedral semiconductors can be calculated using the relation [16],

$$\alpha_L = (0.021/M_P) - D^3(\bar{d} - d_0)^3 \tag{1}$$

where M_P is the semiconductors melting point, d_0 is the mean bonding length for diamond, $\bar{d}$ is the mean bonding length for the material of interest, and D is the slope of $\Delta^{1/3}$ versus d, where $\Delta^{1/3}$ is the cubic root of the difference between the expected α_L calculated from diamond which is equal to $0.021/M_P$ and that obtained by a measurement in the saturation region α_L [17].

The mean bonding length $\bar{d}$ was calculated using a relation applicable for the cubic unit cell for the diamond-like structure which is [2]

$$\bar{d} = \frac{a}{4}\sqrt{3} \tag{2}$$

where a is the unit cell lattice parameter. For all structures, the unit cell volume for the compound under investigation was calculated from their lattice constants; then, the volume of the suggested cubic unit cell was obtained which is the volume occupied by eight lattice points since the system belongs to the diamond structure. The volume related to the diamond structure can be obtained by dividing the actual calculated unit cell for the compounds under investigation by Z, which is, for example, 6 for γ-hexagonal and 3 for rhombohedral. The calculated volume per lattice is then multiplied by 8 to have the corresponding volume for the diamond-like cubic structure [14,16]. The results of these calculations are shown in the last column of Table 1. In this work values obtained for $\bar{d}$, calculated from the lattice constants were used for calculating the lattice thermal expansion. Values of $\Delta^{1/3}$, M_P, and α_L are reported in Table 2. Then the mean experimental lattice thermal expansions α_L for hexagonal as well as Wurtzite structures were calculated from their experimental lattice thermal expansion along the a-axis as α_{La} and the c-axis as α_{Lc}. Figure 1 shows $\Delta^{1/3}$ versus

Table 1 Lattice spacing, mean bonding length, and the crystal structure for some binary defect tetrahedral compounds from the III_2–VI_3 group

Compounds	Crystal structure	a (Å)	c (Å)	Reference	$\bar{d}$ (Å)
Ga_2Se_3	Sphalerite	5.428		[18]	2.3495
$(Ga_{0.6}In_{0.4})_2Se_3$	Sphalerite	5.548		[18]	2.4023
	Hexagonal	6.844	19.324	[18]	2.418
$(Ga_{0.4}In_{0.6})_2Se_3$	Hexagonal	6.98	18.98	[18]	2.434
$(Ga_{0.25}In_{0.75})_2Se_3$	Hexagonal	7.043	19.13	[18]	2.457
In_2Se_3	α-Hexagonal	4.025	19.235	[17]	2.4446
	β-Hexagonal	4.00	28.33	[17]	2.4197
	γ-Hexagonal	7.13	19.58	[17]	2.496
	δ-Hexagonal	4.014	9.641	[17]	2.4419
In_2S_3	α-Tetragonal	7.618	32.295	[19]	2.33
	β-Tetragonal	10.585			2.318
	γ-Octahedral	3.8	9.04		2.308
Al_2S_3	Wurtzite	3.58	5.83	[21]	2.19
Al_2Se_3	Wurtzite	3.89	6.30	[22]	2.375
Al_2Te_3	Sphalerite	5.181		[4]	2.243
Ga_2Te_3	Sphalerite	5.886		[3,23]	2.549
In_2Te_3	Tetragonal	6.173	12.438	[24]	2.679
	Sphalerite	6.158		[4]	2.666
Ga_2S_3	Zincblend	5.17			2.239
Ga_2S_2Te	Tetrahedral	7.09	10.21	[25]	2.4038

the mean atomic distance $\bar{d}$ for all investigated compounds related to the defect group of III_2–VI_3 along with that of the group IV semiconductors where the straight line should pass the $\bar{d}$ axis at a value that belongs to diamond which is 1.545 Å.

As mentioned earlier, Eq. 1 requires two conditions: first, the compounds should have the same ionicity and the second is that, the three parameters α_L, M_P, and $\bar{d}$ should belong to the same crystal structure phase of the compound [16]. That means, for a certain group such as III_2–VI_3, the same ionicity is applicable, and for a certain compound, the same crystal structure should be applicable during heating to its melting point or the phase transition temperature which is applicable for many compounds from this group having a structure change during heating. The latter means that α_L should belong to the related crystal structure when the material is melted or the structure is changed. When the compounds undergo a structure change during heating, then both $\bar{d}$ and α_L used in the calculation should belong to the structure where the melting or structure change occurred. Then, for such compounds and alloys, the phase transition temperature can be taken as the melting point when Eq. 1 is applied. That is the case for many compounds that belongs to the binary group III_2–VI_3 as well as their alloys [8,17,19,20]. Calculated values of the lattice thermal expansion reported in Table 2 were obtained, using Eq. 1, from values of the melting point or phase transition temperature. The latter is for compounds and alloys facing a structure

Table 2 Melting point and experimental and calculated lattice thermal expansion for some binary defect tetrahedral compounds and their alloys from the III_2–VI_3 group

Compounds	M_P (K)	Ref.	α_a (10^{-6} K^{-1})	α_c (10^{-6} K^{-1})	Ref.	α_L (10^{-6} K^{-1}) (Exp.)	$\Delta^{1/3}$ (10^{-6} K$^{-1/3}$)	α_L (10^{-6} K^{-1}) (Eq. 5)
Ga_2Se_3	1293	[18]	10.2		[17]	10.2	1.82	10.06
$(Ga_{0.6}In_{0.4})_2Se_3$	1143	[18]	11.1		[17]	11.1	1.937	10.89
$(Ga_{0.6}In_{0.4})_2Se_3$	1093[a]	[18]	13.8	7.8	[17]	11.8	1.949	11.31
$(Ga_{0.4}In_{0.6})_2Se_3$	1103	[18]	4.7	38	[17]	13.76	1.74	10.7
$(Ga_{0.25}In_{0.75})_2Se_3$	1130	[18]	5.35	32	[17]	14.15	1.64	9.58
α-In_2Se_3	473[a]	[17]			[28]			35.7
β-In_2Se_3	793[a]	[17]						18.54
γ-In_2Se_3	1003[a]	[17]	5.1	16.3	[18]	8.67	2.30	10.72
δ-In_2Se_3	1153	[17]						9.65
In_2S_3	693	[19]	15	15		15	2.48	24.56
	1023		13			13	1.96	15.04
	1363						1.69	10.13
Al_2S_3(Wur.)	1403	[4]						11.78
Al_2Se_3	1253	[4]						9.97
Al_2Te_3(Sph.)	1168	[4]						13.9
Ga_2Te_3	1063	[4]	8.3		[29]	8.3	2.254	7.74
In_2Te_3(Tetra.)	823[a]	[25]	10.3			10.3	2.48	8.44
(Sph.)	940	[25]						5.62
Ga_2S_3	1360	[26]						11.46
Ga_2S_2Te	1123	[27]						11.18

[a] Reported phase transition temperature

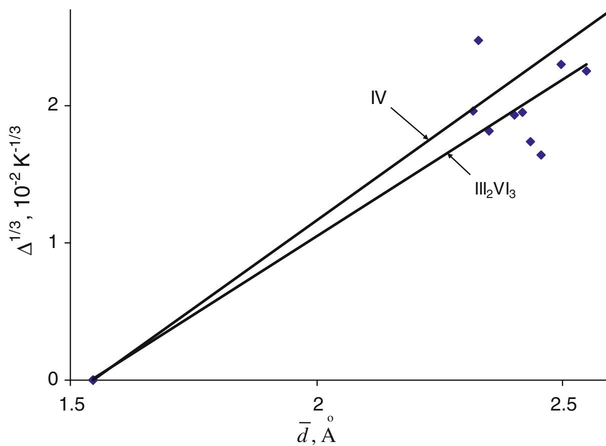

Fig. 1 Cubic root of the deviation of the lattice thermal expansion of a semiconductor from that of the expected value of diamond versus mean bonding length for some compounds from group III_2–VI_3 semiconductors compared to that of group IV semiconductors before applying the effect of both ionicity and crystal structure

change during heating where they are marked by ([a]) in Table 2. Values of $\bar{d}$ which are reported in Table 1 are calculated from their related structure phase.

In Fig. 1, there are points with a large deviation from the fitting curve in comparison with those reported for compounds that belong to groups IV, III–V, II–VI, and the ternary reported in Refs. [14] and [15]. The difference is that many of the compounds from group III_2–VI_3 have structure changes during their heating. For example, the crystal structure for In_2Se_3 changes four times [17] and In_2S_3 three times [18] before reaching their melting points. The lattice thermal expansion for β-In_2S_3 is $13 \times 10^{-6}\,K^{-1}$ for cooling and $35 \times 10^{-6}\,K^{-1}$ for heating [20] where the first results in $\Delta^{1/3}$ versus $\bar{d}$ points are higher than the fitting curve, while the second results in them at a lower position. The actual lattice thermal expansion should then fall between the two values as indicated in Table 2. However, the lattice thermal expansion has been measured for the Ga_2Se_3–In_2Se_3 alloy system on heating [17] and that is why the alloyed side of the In_2Se_3 compound has higher values of the thermal expansion which explains the deviations of its $\Delta^{1/3}$ to lower values. With respect to the explanation above, the method used in this work can be recommended for calculating the lattice thermal expansion particularly for compounds having a phase transition during their heating.

Values of D for a certain group of semiconductors give a suggestion of the degree of stability for the crystal structure of compounds as well as their preparation simplicity [14,15]. According to this standard, the value of D for III_2–VI_3 which is 0.02281 indicates that compounds from this group are more stable and easier in their preparation, especially as a single crystal than those that have D values higher than 0.02281 [14,15]. However, depending on this conclusion, the preparation of thin films for compounds from group III_2–VI_3 are easier than for those compounds that belong to the ternary group II–IV–V_2, while they are more difficult in preparation than compounds from groups of III–V, II–VI, and I–III–VI_2 [14].

In my previous studies [14,15], the equation for calculating the lattice thermal expansion applicable for binary and ternary tetrahedral compound semiconductors having different ionicities was found and reported in the form,

$$\alpha_\mathrm{L} = \frac{0.021}{M_\mathrm{P}} - \left[0.0256\left[\left[\{m(\Delta CA_1) + n(\Delta CA_2)\}\right.\right.\right.$$
$$\left.\left.\left. - \left\{(\Delta A_1A_2) + x^{-0.91}\Delta[A_1 - (\Delta A_1A_2)]^{2.685}\right\}\right]\frac{1}{q}\right]^{-1/3.5}(d - 1.545)\right]^3 \tag{3}$$

In this equation, A_1 and A_2 are the number of valence electrons for the first and second cations in the ternary compounds. For binary compounds from the III_2–VI_3 group, A_1 is for the cation from group III elements and A_2 is for the vacancy. The symbol C represents the number of valence electrons in the anion atoms; in this case and for the present group, m is the number for the first cation type atoms of group III which is 2 and n is the number for the second cation which is the vacancy and is equal to 1. The parameter ΔCA_1 is the valence electron difference between C and A_1, the other Δ's in the equation have the same meaning, while x is the difference between the two types of cation lattice numbers and is equal to 1 for the III_2–VI_3 group compounds where the details are given elsewhere [15]. The parameter q in the equation is the number of cation or anion lattices and is equal to 3 for this group of compounds. For defect tetrahedral structure compounds, another parameter should be added to Eq. 3 to the part which is related to the ionicities that belong to the difference in the cation lattices which is $x^{-0.91}\,[\Delta[A_1 - (\Delta A_1A_2)]]^{2.685}$. Through the method of trial and error, the solution to Eq. 3 for finding the lattice thermal expansion for defect tetrahedral compounds from the III_2–VI_3 group was obtained when the parameter p is added to the latter part which has the form $x^{-0.91}\left[\Delta\left[A_1 - (\Delta A_1A_2) + p^{0.51}\right]\right]^{2.685}$, where p is the number of valence electrons for the missed base vacant atom and is equal to 3 for this group of binary compound semiconductors. Then, the correction parameter to bring the value of D for the group of III_2–VI_3 compounds exactly to that of group IV is

$$\left[\left[\{m(\Delta CA_1) + n(\Delta CA_2)\}\right.\right.$$
$$\left.\left. - \left\{(\Delta A_1A_2) + x^{-0.91}\Delta\left[A_1 - (\Delta A_1A_2) + p^{0.51}\right]^{2.685}\right\}\right]\frac{1}{q}\right]^{1/3.5}$$

This correction parameter will bring $\Delta^{1/3}$ versus $\bar{d}$ that is plotted in Fig. 1 to exactly that of group IV as shown in Fig. 2. Then Eq. 3 takes the form,

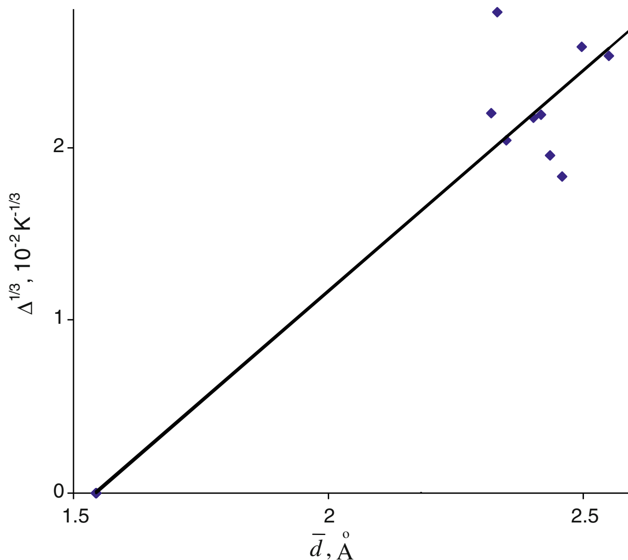

Fig. 2 Cubic root of the deviation of the lattice thermal expansion of a semiconductor from that of the expected value of diamond versus mean bonding length after applying the effects of ionicity for the compounds of III_2–VI_3 group compared to that of group IV semiconductors

$$\alpha_L = \frac{0.021}{M_P} - \left[0.0256\left[\left[\{m(\Delta CA_1) + n(\Delta CA_2)\} - \left\{(\Delta A_1 A_2) + x^{-0.91}\Delta\left[A_1 - (\Delta A_1 A_2) + p^{0.5}\right]^{2.685}\right\}\right]\frac{1}{q}\right]^{-1/3.5}(d - 1.545)\right]^3 \quad (4)$$

In Eq. 4 A_1 and A_2 are valence electrons for the first and second cation type atoms where the second is the vacancy and has zero valence electrons. Equation 4 is a general relation applicable to calculate the lattice thermal expansion for the binary defect group compounds III_2–VI_3 and all the groups given in [1,2]. Values of α_L for compounds that belong to the binary group III_2–VI_3 and their alloys were calculated using Eq. 4 and are given in Table 2.

For calculating the mean ionicity of the group compounds, the equation below that was modified by Omar [14] for tetrahedral compounds was used,

$$D = \left(b_0 \pm b_1 \bar{f}_i^2\right)^{1/3} \quad (5)$$

where $\bar{f}_i$ is the mean ionicity and is the arithmetic mean of the ionicity of all compounds of a given family, and b_0 and b_1 are constants representing values obtained from the curve fitting in Fig. 3 as D^3 versus $\bar{f}_i^2$. The best values for these two constants were found to be $16.72 \times 10^{-6}\,K^{-1/3} \cdot Å^{-1}$ and $28.20 \times 10^{-6}\,K^{-1/3} \cdot Å^{-1}$, respectively.

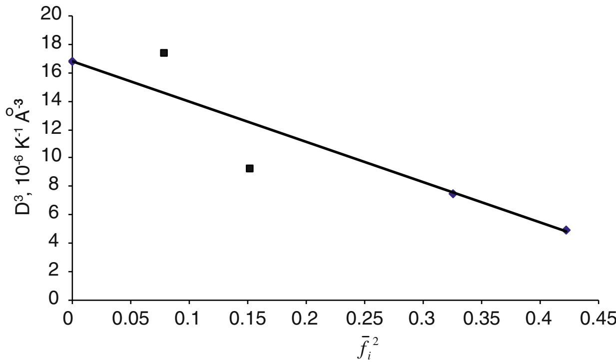

Fig. 3 D^3 in $K^{-1/3} \cdot Å^{-1}$ versus $\bar{f}_i^2$ "square of mean ionicity" for several normal tetrahedral compound semiconductors

Table 3 Values of D in $K^{-1/3} \cdot Å^{-1}$ "the slope of $\Delta^{1/3}$ versus mean bonding length" and $\bar{f}$ "experimental and calculated mean ionicity" for nine groups of normal and defect tetrahedral compound semiconductors

Compound groups	D ($K^{-1/3} \cdot Å^{-1}$)	$\bar{f}_i$ (from experiment)	$\bar{f}_i$ (calculated)	$\bar{f}_i$ (this work)
IV	0.0256 [14]	0.0 [30]		0.00
III–V	0.0210 [14]	0.39 [30]		0.516
II–VI	0.0170 [14]	0.65 [30]		0.648
II–IV–V_2	0.0259 [14]	0.28 [30]		0.147
I–III–VI_2	0.0196 [14]	0.57 [30]		0.572
I–IV_2–V_3	0.0281 [14]		0.442 [14]	0.439
I_2–IV–VI_3	0.02675 [15]		0.323 [15]	0.290
I_3–V–VI_4	0.03195 [15]		0.785 [15]	0.750
III_2–VI_3	0.02281 [this work]			0.416

These two values in Eq. 5 will give ionicities for III_2–VI_3 and other ternary, binary, and elementary group compounds as given in Table 3. However, different values for b_0 and b_1 in the range $(16.76–17.06) \times 10^{-6}\,K^{-1/3} \cdot Å^{-1}$ and $(26.35–29.86) \times 10^{-6}\,K^{-1/3} \cdot Å^{-1}$, respectively, have been reported elsewhere [14,15]. This range of values for b_0 and b_1 in Eq. 5 will give the change in the calculated ionicity values by about ± 0.033. In Eq. 5, the positive sign is for the group compounds having values of D higher than that of group IV, which is 0.0256, while the negative sign is for smaller D values, which is also applicable for group compounds of interest in this work. According to Eq. 5, the calculated value for the mean ionicity in II_2–VI_3 group compounds is 0.416 which is lower than for group IV semiconductors.

3 Conclusions

A modified general formula for calculating the lattice thermal expansion from the melting point and the mean bond length for normal tetrahedral compound semiconductors can be made applicable for binary defect tetrahedral compounds from the III_2–VI_3

group. For compounds having structure changes during heating, the phase transition temperature can be regarded as the melting point for the related structure for which the thermal expansion is known. The idea may be extended to investigate the expected phase transition for compounds having their structure change during heating.

Acknowledgments I would like to thank S. R. Saeed, from the Department of Physics of nanostructure and nanotechnology, Jagiellonian University in Poland for his assistance in the data collection and to College of Science, University of Salahaddin in Arbil, Iraqi Kurdistan, for financial support.

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