The Relationship Between Atomic Packing Density and the Gruneisen Parameter in $(TlGaSe_2)_{1-x}$-$(TlInS_2)_x$ (x=0.1, 0.2) Solid Solutions

A.M.Akhmedova [1*] S.Z. Dzhafarova [1] and Ulviya Bunyatova [2]

[1]Department of Engineering and Applied Sciences, Azerbaijan State University of Economics Baku, Azerbaijan
[2] Biomedical Department, Baskent University, Ankara, Turkey
Ahmadova_Arzu@unec.edu.az

Abstract. In this study, the value of the Gruneisen parameter calculated based on the experimental values of the thermal expansion and isothermal compression coefficients of the $(TlGaSe_2)_{1-x}$-$(TlZnS_2)_x$ (x=0.1, 0.2) solid solution, as well as the specific heat capacity at constant volume, is given in the form of a table. Through the existing thermodynamic relations, it has been determined that there is a direct relationship between the Gruneisen parameter and the packing density of atoms in the crystal lattice. The values of both parameters calculated by various methods are also given in the form of a table. Certain suggestions have been made regarding the usefulness of the existing thermodynamic relations for complex semiconductors.

Keywords: Solid Solution, Thermal Expansion, Isothermal Compression, Specific Heat Capacity, Crystal Structure, Lattice Parameter, Packing Density, Gruneisen Parameter

1. Introduction

$(TlGaSe_2)_{1-x}$-$(TlInS_2)_x$ (x=0.1; 0.2) solid solutions belong to the group of semiconductors that crystallize in layered and chain structures. $(TlGaSe_2)_{1-x}$-$(TlInS_2)_x$ solid solutions are interesting materials both from the point of view of theoretical and practical applications and are also interesting in terms of testing existing theoretical models related to the temperature dependences of thermal and elastic parameters. Such complex compounds and solid solutions are used in the preparation of the main elements of semiconductor laser devices, as well as in the preparation of sensitive semiconductor converters. In the construction of the thermodynamics of such complex semiconductors, it is also important from a theoretical point of view to verify the existing thermodynamic relations between thermal parameters and empirical formulas.

The thermodynamic relationship between the thermal parameters of solids is determined by the value of the Gruneisen parameter (γ_Q), which is an indicator of the degree of anharmonicity of the oscillations of atoms in the crystal lattice. Knowing the

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value of this parameter, it is possible to make certain predictions in advance about the temperature dependence of the thermal expansion coefficient (α), specific heat capacity (c_P), and isothermal compression coefficient (χ_T) of the material under study [1, 2, 9].

2. Results and Discussion

Using the existing relationships between thermal parameters, it is also found that there is a direct relationship between the Gruneisen parameters, which indicates the degree of anharmonicity of the oscillation of atoms in the crystal lattice, and the packing density (a) of atoms in the crystal lattice [3, 4, 8].

Thus,

$$\frac{c_P}{c_V} = 1 + \frac{3\alpha T}{a} \quad (1)$$

$$c_P - c_V = \frac{9\alpha^2 VT}{\chi_T} \quad (2)$$

$$\gamma_Q = \frac{3\alpha V}{\chi_T \cdot c_V} \quad (3)$$

by solving the expressions together, we get

$$a = \frac{1}{\gamma_Q} \quad (4)$$

In these expressions, c_P and c_V are the specific heat capacities at constant pressure and constant volume, x-the coefficient of linear thermal expansion, χ_T- the coefficient of isothermal compression, V- the molar volume, T- the absolute temperature, and a - the packing density of atoms in the crystal lattice.

In this work, the Gruneisen parameter and the pacing density of atoms in the crystal lattice were calculated using experimental values of thermal parameters in $(TlGaSe_2)_{1-x}$-$(TlInS_2)_x$ (x=0.1, 0.2) solid solutions.

Based on the existing methodology, the studied solid solutions were synthesized, and single crystals were obtained [5, 9]. Their perfection and type of crystal structure were determined by X-ray analysis. It was found that both compounds crystallize in the monoclinic structure, and the lattice parameters are as follows:

for $(TlGaSe_2)_{0.9}(TlInS_2)_{0.1}$ composition: a=10.765 Å; b=10.558 Å; c=15.635 Å; β=100.6^0,

for $(TlGaSe_2)_{0.8}(TlInS_2)_{0.2}$ composition: a=10.531 Å; b=10.598 Å; c=15.632 Å; β=100.6^0.

The comparison shows that as the weight ratio of the $TlInS_2$- compound in the composition of the solid solutions studied increases, a partial change occurs in the value of the lattice parameters. In order to determine the effect of such a change on the value of the interatomic chemical bond, the possible phase transition in the composition, as well as on the thermal parameters, the thermal expansion (α) and isothermal compression coefficients (χ_T) of the $(TlGaSe_2)_{1-x}$-$(TlInS_2)_x$ (x=0.1; 0.2) solid solutions were measured. For the measurements, cylindrical samples with a diameter of $5\cdot10^{-3}$ m and a height of $3\cdot10^{-2}$ m were prepared from the synthesized compositions. The measurements were carried out based on the methodology available in the literature [2, 9]. The relative error of the experiment was 0.5%.

Using the values of the thermal expansion coefficient given in the table for both compositions, the ratio of the degree of anharmonicity of atoms in the crystal lattice to the square of the degree of harmonicity γ/β^2 was calculated (Table 1).

Table 1.

T, K	*$(TlGaSe_2)_{0,9}(TlInS_2)_{0,1}$*		*$(TlGaSe_2)_{0,8}(TlInS_2)_{0,2}$*	
	$\gamma/\beta^2\cdot10^5$, N^{-1}	S_T-S_0, J/mol·K	$\gamma/\beta^2\cdot10^5$, N^{-}	S_T-S_0, J/mol·K
90	3781	0,342	3785	0,21
100	5830	0,9	5814	0,56
120	6318	1,27	6287	0,79
140	5678	1,18	5668	0,72
160	5950	1,446	5942	0,924
180	6288	1,83	6265	1,11
200	7714	3,07	7683	1,9
250	8328	4,49	8355	2,81
300	8597	5,59	8578	3,7

The calculation was carried out based on the formula

$$\alpha = \frac{\gamma k}{a\beta^2}$$

available from the literature [3]. Here, a is the lattice parameter, k is the Boltzmann constant. The results of the calculations are given in table 1.

The values of thermal expansion (α) and isothermal compression coefficients (χ_T) calculated because of measurements are given in the figure (figure 1) and in the table 2, respectively.

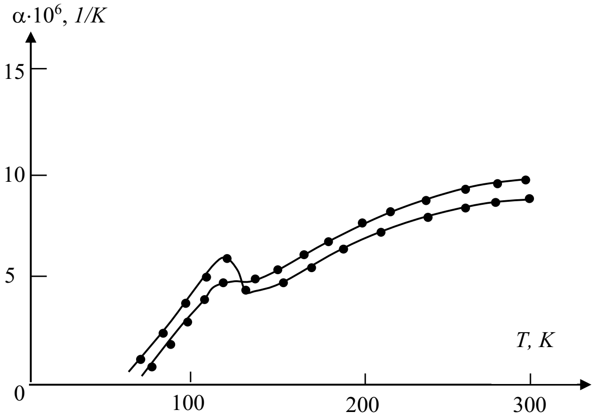

Figure 1. Temperature dependence of the coefficient of thermal expansion of solid solution $(TlGaSe_2)_{1-x}$-$(TlInS_2)_x$ *x*: 1 – 0.1; 2 – 0,2

The value of specific heat capacity (c_P) at constant pressure was found from expression

$$c_p = \frac{9\alpha^2 V T_{mt}}{0.0214\chi_T} \quad (5)$$

obtained from a comparison of the existing thermodynamic and Nernst-Lindeman formulas for the (c_p-c_V) difference.

Here T_{mt} are the melting temperatures of the individual components. These values obtained for c_P - are also given in Table 2.

Table 2

T, K	$(TlGaSe_2)_{0.9}(TlInS_2)_{0.1}$					
	$\alpha \cdot 10^{-6}$, 1/K	$\chi_T \cdot 10^{-12}$ m^2/N	C_p, j/kg·K	$(C_p$-$C_V)$, j/kg·K	C_V, j/kg·K	γ_Q
90	4,96	6,37	98,41	0,30	98,11	1,888
100	7,65	6,46	159,32	0,68	158,64	1,776
120	8,29	6,48	167,42	0,84	166,58	1,789
140	7,45	6,59	152,41	0,76	151,65	1,761
160	7,81	6,68	152,88	1,07	151,81	1,760
180	8,25	6,70	169,15	1,35	167,80	1,765
200	10,12	6,72	203,75	2,22	201,53	1,766
250	11,02	6,75	212,22	2,93	209,28	1,782
300	11,28	6,78	224,25	3,32	220,93	1,783
T, K	$(TlGaSe_2)_{0.8}(TlInS_2)_{0.2}$					
	$\alpha \cdot 10^{-6}$, 1/K	$\chi_T \cdot 10^{-12}$ m^2/N	C_p, j/kg·K	$(C_p$-$C_V)$, j/kg·K	C_V, j/kg·K	γ_Q
90	4,95	6,32	100,85	0,31	100,54	1,993
100	7,62	6,45	164,95	0,69	164,26	1,806
120	8,24	6,46	173,30	0,87	172,43	1,865
140	7,43	6,54	155,77	0,78	154,99	1,869
160	7,79	6,63	153,69	1,35	152,34	1,974
180	8,21	6,65	170,41	1,36	169,05	1,872
200	10,07	6,70	204,76	2,23	202,53	1,887
250	10,95	6,68	222,05	3,07	218,98	1,965
300	11,24	6,71	226,88	3,36	223,52	1,937

One of the main issues raised in this work was to examine the dependence of the Gruneisen parameter (γ_Q) on the packing density of atoms in the crystal lattice in the solid solutions studied. For this purpose, using the values of (α), (χ_T) and (c_p) given in the table, the values of the Gruneisen parameter and the packing density of atoms in the crystal lattice were also determined and are given in a separate table for comparison of the obtained results (Table 3).

Table 3

T, K	$(TlGaSe_2)_{0.9}(TlInS_2)_{0.1}$		$(TlGaSe_2)_{0.8}(TlInS_2)_{0.2}$	
	A	γ_Q	*A*	γ_Q
90	0,556	1,798	0,557	1,750
100	0,565	1,775	0,567	1,759
120	0,586	1,703	0,586	1,701
140	0,525	1,902	0,527	1,702
160	0,539	1,851	0,540	1,829
180	0,544	1,832	0,546	1,818
200	0,559	1,784	0,560	1,780
250	0,570	1,750	0,572	1,742
300	0,571	1,751	0,573	1,733

As can be seen from the tables, the thermal expansion, isothermal compression, and specific gravity of the studied solid solution are directly related to the degree of anharmonicity of the thermal oscillations of atoms in the crystal lattice.α, χ_T and c_P the increase in parameters with increasing temperature can be attributed to the weakening of the chemical bond strength between atoms.This weakening also affects the degree of anharmonicity of the oscillations of atoms. The weakening of the chemical bond between atoms in the crystal lattice also leads to a change in the packing density of atoms in that lattice.

If we look at the values in the table, we can see that the specific heat capacities at constant pressure and constant volume of the studied solid solution differ little from each other. Their temperature dependences are also approximately the same. At the same time, one of the interesting results obtained is that in this type of complex compounds and solid solutions, the ratio c_P/c_V is very small and increases slightly with increasing temperature (varying between 1.003 and 1.015).

As the weight ratio of the compound in the $TlInS_2$ composition of the studied solid solution increases, the values of all thermal parameters also change. In other words, there is a slight increase in the values of the α, χ_T and c_P parameters.

3. Conclusion

This suggests that as the amount of the compound in a solid solution $(TlGaSe_2)_{1-x}$-$(TlInS_2)_x$ increases $TlInS_2$, the chemical bonds between atoms weaken.

One of the interesting results obtained during the research is that, as shown in theoretical models, there is a direct relationship between the degree of anharmonicity of the oscillations of atoms in the crystal lattice and the packing density of atoms in the lattice. In other words, expression (4) is satisfied within the experimental error.

Thus, as a final conclusion, it can be said that by changing the weight ratio of the compound $(TlGaSe_2)_{1-x}(TlInS_2)_x$ in the composition of the solid solution $T\ell InS_2$, the value of the thermal parameters can be changed in the necessary direction from the point of view of practical application.

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