IJCRT.ORG ISSN : 2320-2882

INTERNATIONAL JOURNAL OF CREATIVE RESEARCH THOUGHTS (IJCRT)

An International Open Access, Peer-reviewed, Refereed Journal

Analysis Of Volume Dependence Of Grüneisen Parameter And Melting Curves For Some Binary Solids

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Abstract

We have investigated the volume dependence of Grüneisen parameter and melting curves of some binary ionic and partially covalent solids viz. NaCl, NaF, LiF, MgO, CaF_2, SiC. We make use of the generalized free-volume formula and Burakovsky-Preston model for determining gamma for solids at different values of volume compressions. The Burakovsky-Preston model has been reformulated here used in the Lindemann law in order to predict melting curves of binary solids. The calculated values present close agreement with a available experimental data.

Keywords : Binary solids, Grüneisen parameter, Free-volume formula, Burakovsky - Preston model, Lindemann law of melting.

Introduction

It should be imphasized that the Grüneisen parameter gamma is an important physical quantity which is related to thermoelastic property such as thermal expansivity, bulk modulus specific heat of solids. We have following relationship (Anderson, 1995, Stacey and Davis, 2004, Stacey, 2005).

$$\gamma = \frac{\alpha K_T V}{C_V} = \frac{\alpha K_S V}{C_P} \quad (1)$$

where α is thermal expansivity

$$\alpha = \frac{1}{V}\left(\frac{dV}{dT}\right)_P \quad (2)$$

where K_T and K_S are respectively the isothermal and adiabatic bulk moduli

$$K_T = -V\left(\frac{dT}{dV}\right)_T \quad (3)$$

and

$$K_S = -V\left(\frac{dP}{dV}\right)_S \quad (4)$$

we make use of the following generalized free-volume formula (Vashchenko and Zubarev, 1963). Which can be written as follows

$$\gamma = \frac{\frac{K'}{2} - \frac{1}{6} - \frac{f}{3}\left(1 - \frac{P}{3K}\right)}{1 - 2f\frac{P}{3K}} \quad (5)$$

where f is the free-volume parameter. Different formulations (Barton and Stacey, 1985; Dugdale and MacDonald, 1953; Slater, 1939; Vashchenko and Zubarev, 1963) were developed for γ by taking f equal to 0, 1, 2, and 2.35. Value of f can also be determined by matching the zero pressure value of γ for the given material. Values of pressure P, bulk modulus K and pressure derivative of bulk modulus K' are determined using the Holzapfel AP2 EOS (Holzapfel, 1998).

2. Method of Analysis

Values of gamma are determined using the generalized free-volume formula given by Eq. (5). Where used the Holzapfel AP2 EOS based on the Thomas-Fermi model taking K'_∞ =5/3 in the limit of extreme compression. This EOS is given below (Holzapfel, 1998; Sunil et al., 2024).

$$P = 3K_0 x^{-5}(1-x)[1+C_2 x(1-x)]\exp[C_0(1-x)] \tag{6}$$

where $x = (V/V_0)^{1/3}$, K_0 is the value of bulk modulus K at P = 0, and

$$C_0 = -\ln\left(\frac{3K_0}{P_{FG0}}\right) \tag{7}$$

$$P_{FGO} = a_{FG}\left(\frac{Z}{V_0}\right)^{5/3} \tag{8}$$

and

$$C_2 = \frac{3}{2}(K'_0 - 3) - C_0 \tag{9}$$

Here K'_0 is the pressure derivative of bulk modulus, $K' = dK/dP$ at zero-pressure. Eq. (6) gives a correct Thomas-Fermi limit of pressure at extreme compression. The results alongwith the values of input data are given in Table 1 and 2.

In order to investigate the values of gamma in terms of V/V_0 we have used the formula (Burakovsky and Preston, (2004) given below

$$\gamma = \gamma^\infty + A_1\left(\frac{V}{V_0}\right)^{1/3} + A_2\left(\frac{V}{V_0}\right)^m \tag{10}$$

where A_1, A_2 and m are constants for a given material. We can assume that $A_1 = A_2$ is Eq. (10). Then at P = 0, V = V_0, $\gamma = \gamma_0$

We have from Eq. (10)

$$A_1 = A_2 = \frac{1}{2}\left(\gamma_0 - \frac{1}{2}\right) \tag{11}$$

By fitting values of gamma determined from the generalized free-volume formula, we obtain different values of m for different materials given in Table 1. Now we use the Burakovsky-Preston model, Eq. (11), in the Lindemann law of melting given below -

$$\frac{d\ln T_m}{d\ln V} = -2\left(\gamma - \frac{1}{3}\right) \tag{12}$$

Using Eq. (10) in Eq. (12) and then integrating, we get

$$T_m = T_{m_0}\left(\frac{V}{V_0}\right)^{-1/3}\exp\left[6A_1\left\{1-\left(\frac{V}{V_0}\right)^{1/3}\right\} + \frac{2A_1}{m}\left\{1-\left(\frac{V}{V_0}\right)^m\right\}\right] \tag{13}$$

We have calculated T_m at different values of V/V_0 for the six binary materials. The results are given in Table 3. In the limit of extreme compression $V \to 0, P \to \infty$ and therefore, we have (Shanker et al., 2020).

$$T_{m\infty} = \text{infinity} \tag{14}$$

Values of T_m versus V/V_0 have transformed to the corresponding values of T_m versus pressure P using the Holzapfel AP2 EOS.

3. Discussion and Conclusions

We have use the Holzapfel AP2 EOS for predicting pressure, bulk modulus and its pressure derivative for solids under study. These results are used in the generalized free volume formula to obtain γ. The Burakovsky-Preston model is then used to determine the parameters of the model taking values of γ. An important results, $\gamma_\infty = 1/2$, has been used here to determine values of model parameters. The Grüneisen parameter decreases with the increase in volume compression. The melting temperatures at different pressures have been calculated using Eq. (13) based on the Lindemann law and the Burakovsky-Preston model.

The results for NaCl upto pressures less than 30 GPa are given in Table 3. The results for NaCl are found to compare well with the available experimental data, (Boehler et al., 1997) and also with those computed from molecular dynamics simulations (Belonoshko et al., 1996). The results for NaF and LiF, the calculated values experimental data and the molecular dynamics simulations are in close agreement with each other (Boehler et al., 1996; Boehler et al., 1997). The experimental data reported by Zeer and Boehler (1994) give a nearly flat melting curve for MgO which has been challenged by several authors (Anand et al., 2022). Okamoto and Fuchizaki, (2017) have used a one-phase approach based on the earlier formulations (Kumari and Dass, 1988, Kechin, 2001) for predicting melting curve of MgO. They extrapolated melting temperatures at high pressures up to 200 GPa (Okamoto and Fuchizaki, 2017) using the available experimental data for MgO (Zerr and Boehler, 1994). The melting temperature near the Core-mantle boundary (CMB) pressure was nearly 6000 K (Okamoto and Fuchizaki, 2017). The micro-texture analysis was performed by Kimura et al. (2017) to determine melting temperatures of MgO at high pressures which turned out to be much higher than those determined using laser-heated diamond anvil cell.

The value of T_m for MgO at CMB pressure determined from micro-texture analysis is nearly 7900 K (Kimura et al., 2017). The corresponding value of T_m obtained in the present study for MgO at CMB pressure is closer to 7200 K, an average of

that determined (Okamoto and Fuchizaki, 2017) by extrapolating the experiment data (Zerr and Boehler, 1994) and the value based on micro-texture analysis (Kimura et al., 2017).

The results for CaF_2 obtained in the present study agree closely with available experimental data (Cazorla and Errandonea, 2014) and also with the ab initio simulations. The results for SiC are in good agreement with the theoretical results reported recently by Anand et al. (2022) and Sunil et al. (2024).

Table 1 : Values of input data used in calculations taken from Sunil et al. (2024).

	NaCl	NaF	LiF	MgO	CaF_2	SiC
γ_0	1.59	1.72	1.63	1.54	1.90	1.06
$K_0(GPa)$	24.0	46.5	66.5	162	81.7	241
K_0'	5.35	5.28	5.30	4.15	5.22	2.84
f	2.75	2.26	2.56	1.11	1.62	0.58
m	1.83	2.19	2.92	1.50	2.46	0.44
$T_{m_0}(K)$	1074	1266	1118	3063	1660	3100

Table 2 : Results for pressure P, bulk modulus K, pressure derivative of bulk modulus K', and the Grüneisen parameter for some binary solids at different values of volume compression (V/V_0) calculated using the Holzapfel AP2 EOS and generalized free-volume formula.

NaCl				
$\frac{V}{V_0}$	P(GPa)	K(GPa)	K'	γ
1	0	24.0	5.35	1.59
0.95	1.41	31.2	4.95	1.53
0.90	3.34	40.4	4.61	1.47
0.85	5.98	52.2	4.33	1.41
0.80	9.59	67.4	4.09	1.36
0.75	14.6	87.1	3.89	1.32
0.70	21.4	113	3.70	1.26
0.65	31.1	148	3.54	1.22
NaF				
$\frac{V}{V_0}$	P(GPa)	K(GPa)	K'	γ
1	0	46.5	5.28	1.72
0.95	2.73	60.3	4.87	1.64
0.90	6.44	77.7	4.53	1.56
0.85	11.5	99.8	4.25	1.49
0.80	18.4	128	4.01	1.43
0.75	27.8	165	3.80	1.37
0.70	40.8	213	3.61	1.31
0.65	58.8	276	3.45	1.26
LiF				
$\frac{V}{V_0}$	P(GPa)	K(GPa)	K'	γ
1	0	66	5.30	1.63
0.95	3.90	86	4.86	1.54
0.90	9.22	111	4.50	1.46
0.85	16.4	142	4.21	1.39
0.80	26.2	182	3.96	1.33
0.75	39.6	234	3.74	1.26
0.70	57.9	300	3.55	1.18
0.65	83.4	388	3.38	1.15
MgO				
$\frac{V}{V_0}$	P(GPa)	K(GPa)	K'	γ
1	0	162	4.15	1.54
0.95	9.24	199	3.93	1.49
0.90	21.2	245	3.73	1.43
0.85	36.8	302	3.56	1.38
0.80	57.2	373	3.41	1.34
0.75	84.0	462	3.27	1.30
0.70	120	577	3.15	1.26
0.65	168	725	3.04	1.22
0.60	233	921	2.93	1.18

CaF_2				
$\frac{V}{V_0}$	P(GPa)	K(GPa)	K′	γ
1	0	81.7	5.22	1.90
0.95	4.79	106	4.81	1.79
0.90	11.3	136	4.47	1.70
0.85	20.1	174	4.19	1.61
0.80	32.1	222	3.96	1.54
0.75	48.4	285	3.75	1.47
0.70	70.8	367	3.57	1.41
0.65	102	475	3.40	1.34
0.60	145	620	3.26	1.29
SiC				
$\frac{V}{V_0}$	P(GPa)	K(GPa)	K′	γ
1	0	241	2.84	1.06
0.95	13.3	278	2.76	1.04
0.90	29.5	322	2.69	1.03
0.85	49.5	375	2.63	1.02
0.80	74.1	439	2.57	1.00
0.75	105	518	2.52	0.99
0.70	144	615	2.48	0.98
0.65	194	738	2.44	0.97
0.60	259	896	2.40	0.96

Table 3 : Results for volume compression (V/V_0), pressure P, and melting temperature T_m(K).

NaCl		
V/V_0	**P(GPa)**	**Tm(K)**
1	0	1074
0.95	1.41	1218
0.90	3.34	1382
0.85	5.98	1568
0.80	9.59	1786
0.75	14.6	2034
0.70	21.4	2321
0.65	31.1	2656
NaF		
V/V_0	**P(GPa)**	**Tm(K)**
1	0	1266
0.95	2.73	1452
0.90	6.44	1665
0.85	11.5	1909
0.80	18.4	2190
0.75	27.8	2514
0.70	40.8	2888
0.65	58.8	3327
LiF		
V/V_0	**P(GPa)**	**Tm(K)**
1	0	1118
0.95	3.90	1271
0.90	9.22	1442
0.85	16.4	1633
0.80	26.2	1880
0.75	39.6	2090
0.70	57.9	2300
0.65	83.4	2679
MgO		
V/V_0	**P(GPa)**	**Tm(K)**
1	0	3063
0.95	9.24	3458
0.90	21.2	3910
0.85	36.8	4428
0.80	57.2	5028
0.75	84.0	5700
0.70	120	6520

0.65	168	7462
0.60	233	8576
CaF_2		
V/V_0	**P(GPa)**	**Tm(K)**
1	0	1660
0.95	4.79	1940
0.90	11.3	2413
0.85	20.1	2638
0.80	32.1	3073
0.75	48.4	3580
0.70	70.8	4172
0.65	102	4872
0.60	145	5706
SiC		
V/V_0	**P(GPa)**	**Tm(K)**
1	0	3100
0.95	13.3	3473
0.90	29.5	3604
0.85	49.5	3904
0.80	74.1	4243
0.75	105	4629
0.70	144	5069
0.65	194	5580
0.60	259	6176

Acknowledgement

Thanks are due to Professor Jai Shanker for his valuable comments and suggestions.

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