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A MODIFIED FORMULATION BASED ON THE SIMON LAW OF MELTING

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We have derived a modified formulation based on the Simon law of melting for solids under the effect of pressure. We have investigated the pressure dependence of melting temperature for alkali halides with rocksalt structure. The results for melting temperature as a function of pressure have been obtained for sixteen alkali halides by using the modified formulation. The calculated values are found to present close agreement with available experimental data.

KEYWORDS : Melting of alkali halides, Simon's law of melting, pressure dependence of melting temperature.

INTRODUCTION

Melting is a very common phenomenon occurring in nature [1]. Melting takes place as a result of the phase transition [2] from solid state to liquid state at high temperatures. Various attempts have been made [1 – 5] to understand physical mechanisms responsible for melting. It is of great interest to investigate the pressure dependence of melting temperature using a melting law formulation [2].

The melting law which has been widely used in recent literature [6 – 8] as well, is the Simon law [9, 10].

$$\frac{T_m}{T_{m_0}} = \left(1 + A_1 \frac{P}{K_0}\right)^t \quad \ldots (1)$$

where A_1 and t are constants for a given material, T_{m0} is the melting temperature T_m at pressure $P = 0$. K_0 is the bulk modulus at zero pressure. We present an analysis by modifying Eq. (1) for determining pressure dependence of T_m in case of sixteen alkali halides with NaCl structure.

METHODS OF ANALYSIS

The Simon law given by Eq. (1) can be written in a simplified form taking $t = 1$ as follows

$$\frac{T_m}{T_{m_0}} = \left(1 + A_1 \frac{P}{K_0}\right) \quad \ldots (2)$$

Table 1. Values of melting temperature of alkali halides at different pressure

LiF				**LiCl**			
***P*(GPa)**	***P*/K_0**	T_m/T_{m0}	A_1	***P*(GPa)**	***P*/K_0**	T_m/T_{m0}	A_1
0.982	0.0147	1.064	4.387	0.376	0.0126	1.074	5.873
2.24	0.0336	1.143	4.244	0.868	0.0292	1.163	5.595
3.87	0.0581	1.238	4.097	1.51	0.0508	1.272	5.348
6.01	0.0903	1.349	3.864	2.38	0.0801	1.406	5.799
8.88	0.1335	1.489	3.662	3.57	0.1202	1.577	4.801
12.8	0.1924	1.666	3.461	5.24	0.1765	1.797	4.581
18.3	0.2751	1.892	3.242	7.67	0.2584	2.085	4.202
26.4	0.3969	2.190	2.998	11.4	0.3840	2.536	4.002
LiBr				**LiI**			
***P*(GPa)**	***P*/K_0**	T_m/T_{m0}	A_1	***P*(GPa)**	***P*/K_0**	T_m/T_{m0}	A_1
0.268	0.0113	1.080	7.052	0.184	0.0106	1.094	8.867
0.62	0.0263	1.179	6.813	0.428	0.0247	1.210	8.758
1.08	0.0459	1.298	6.507	0.726	0.0420	1.355	8.068
1.7	0.0722	1.447	6.186	1.22	0.0706	1.542	7.645
2.56	0.1088	1.635	5.833	1.88	0.1089	1.785	7.182
3.77	0.1602	1.880	5.488	2.86	0.1657	2.113	6.699
5.54	0.2355	2.203	5.106	4.35	0.2520	2.568	6.200
8.22	0.3494	2.651	4.721	6.8	0.3939	3.235	5.652
NaF				**NaCl**			
***P*(GPa)**	***P*/K_0**	T_m/T_{m0}	A_1	***P*(GPa)**	***P*/K_0**	T_m/T_{m0}	A_1
0.520	0.0111	1.060	5.423	0.244	0.0103	1.066	6.417
1.180	0.0253	1.130	5.169	0.556	0.0234	1.144	6.167
2.040	0.0438	1.217	4.958	0.960	0.0454	1.238	5.876
3.160	0.0679	1.321	4.727	1.490	0.0629	1.352	5.596
4.640	0.0998	1.447	4.480	2.190	0.0924	1.494	5.346
6.660	0.1432	1.605	4.224	3.160	0.1334	1.672	5.037
9.480	0.2039	1.805	3.948	4.510	0.1904	1.908	4.768
13.500	0.2904	2.068	3.677	6.450	0.2723	2.200	4.407
NaBr				**NaI**			
***P*(GPa)**	***P*/K_0**	T_m/T_{m0}	A_1	***P*(GPa)**	***P*/K_0**	T_m/T_{m0}	A_1
0.182	0.0093	1.068	7.311	0.148	0.0099	1.071	7.889
0.416	0.0213	1.148	7.047	0.34	0.0286	1.154	7.000
0.72	0.0369	1.245	6.639	0.59	0.0396	1.256	6.464
1.12	0.0575	1.364	6.330	0.928	0.0624	1.384	6.000
1.66	0.0852	1.510	5.985	1.38	0.0928	1.540	5.818

2.41	0.1237	1.698	5.674		2.02	0.1358	1.742	5.496
3.46	0.1777	1.937	5.293		2.91	0.1472	2.004	5.122
5.02	0.2578	2.257	4.891		4.27	0.2871	2.358	4.731
KF					**KCl**			
***P*(GPa)**	P/K_0	T_m/T_{m0}	A_1		***P*(GPa)**	P/K_0	T_m/T_{m0}	A_1
0.362	0.0119	1.059	5.025		0.195	0.0112	1.059	5.267
0.824	0.0272	1.131	4.816		0.444	0.0255	1.128	4.980
1.42	0.0469	1.217	4.626		0.774	0.0446	1.212	4.753
2.22	0.0734	1.320	4.359		1.21	0.0697	1.315	4.519
3.27	0.1082	1.449	4.140		1.79	0.1031	1.443	4.298
4.72	0.1561	1.610	3.910		2.59	0.1492	1.603	4.044
6.75	0.2233	1.816	3.649		3.72	0.2144	1.808	3.775
9.71	0.3213	2.087	3.383		5.39	0.3106	2.082	3.487
KBr					**KI**			
***P*(GPa)**	P/K_0	T_m/T_{m0}	A_1		***P*(GPa)**	P/K_0	T_m/T_{m0}	A_1
0.176	0.0120	1.059	4.835		0.139	0.0120	1.060	5.034
0.404	0.0275	1.128	4.703		0.319	0.0277	1.132	4.765
0.696	0.0475	1.214	4.484		0.553	0.0480	1.219	4.541
1.09	0.0744	1.317	4.247		0.864	0.0750	1.326	4.346
1.61	0.1099	1.444	4.030		1.29	0.1120	1.457	4.080
2.34	0.1598	1.605	3.805		1.87	0.1624	1.625	3.858
3.37	0.2301	1.811	3.526		2.7	0.2345	1.842	3.598
4.9	0.3346	2.087	3.251		3.95	0.3431	2.133	3.303
RbF					**RbCl**			
***P*(GPa)**	P/K_0	T_m/T_{m0}	A_1		***P*(GPa)**	P/K_0	T_m/T_{m0}	A_1
0.38	0.0142	1.062	4.366		0.206	0.0132	1.060	4.669
0.872	0.0326	1.136	4.250		0.476	0.0305	1.134	4.360
1.52	0.0569	1.226	3.971		0.828	0.0531	1.227	4.180
2.39	0.0895	1.335	3.764		1.3	0.0834	1.332	3.987
3.58	0.1341	1.475	3.544		1.93	0.1238	1.468	3.796
5.26	0.1971	1.652	3.304		2.82	0.1810	1.641	3.535
7.67	0.2874	1.884	3.080		4.1	0.2631	1.866	3.292
11.3	0.4235	2.201	3.839		6.02	0.3863	2.170	3.031
RbBr					**RbI**			
***P*(GPa)**	P/K_0	T_m/T_{m0}	A_1		***P*(GPa)**	P/K_0	T_m/T_{m0}	A_1
0.179	0.0135	1.063	4.769		0.124	0.0118	1.061	5.563
0.412	0.0311	1.137	4.419		0.284	0.0270	1.134	4.962
0.714	0.0539	1.231	4.285		0.495	0.0471	1.221	4.692

1.12	0.0845	1.339	4.035		0.775	0.0738	1.332	4.501
1.67	0.1261	1.477	3.782		1.16	0.1105	1.465	4.212
2.44	0.1842	1.653	3.548		1.69	0.1611	1.639	3.968
3.53	0.2666	1.881	3.299		2.45	0.2335	1.863	3.703
5.17	0.3904	2.188	3.646		3.6	0.3431	2.165	3.396

It is found that A_1 does not remain constant with the change in pressure when Eq. (2) is fitted to experimental data on melting curves [11, 12]. Sunil *et al*. [13] have reported the data on melting temperatures for sixteen alkali halides under the effect of pressure. They have also extraploted the values of melting data by using the formulation of Lindemann's law based on the volume dependence of the Grüneisen parameter [14 – 16]. We make use Simon's law in case of alkali halides which are strongly ionic crystals. By fitting Eq. (2) to melting data [13] we determine values of A_1 which are given in Table 1 alongwith the data used. It is found from Table 1 that A_1 does not remain constant but changes significantly with the increase in pressure. In fact, we find the following relationship to satisfy the variations in A_1 with pressure

$$A_1 = A_0\left(1 - x\frac{P}{K_0}\right) \quad \ldots (3)$$

Best fit values of parameters A_0 and x are reported in Table 2. Eqs. (2) and (3) then yield the following modified formula for the Simon melting law

$$\frac{T_m}{T_{m_0}} = 1 + A_0\left(1 - x\frac{P}{K_0}\right)\frac{P}{K_0} \quad \ldots (4)$$

Values of T_m have been calculated with the help of Eq. (4) using A_0 and x given in Table 2.

Table 2. Calculated values of parameters A_0 and x (Eq. 3)

Crystal	A_0	x		**Crystal**	A_0	x
LiF	4.44	0.818		**NaF**	5.49	1.139
LiCl	5.93	0.848		**NaCl**	6.49	1.181
LiBr	7.12	0.966		**NaBr**	7.40	1.357
LiI	8.88	0.935		**NaI**	8.00	1.423
Crystal	A_0	x		**Crystal**	A_0	x
KF	5.09	1.042		**RbF**	4.39	0.844
KCl	5.34	1.114		**RbCl**	4.73	0.928
KBr	4.89	1.003		**RbBr**	4.81	0.619
KI	5.10	1.135		**RbI**	5.64	1.159

Results and discussions

The results for sixteen alkali halides obtained from Eq. (4) are given in Table 3. These are compared with the corresponding values [13] based on the experimental data [11, 12] and extrapolated using the Lindemann law

Table 3. Comparison of the results for melting temperature of alkali halides (a) calculated from Eq. (4), and (b) experimental data [13]

LiF				**LiCl**		
***P*(GPa)**	***Tm***			***P*(GPa)**	***Tm***	
	(a)	**(b)**			**(a)**	**(b)**
0	1115	1115		0	887	887
0.982	1184	1187		0.376	953	953
2.24	1276	1274		0.868	1036	1032
3.87	1388	1381		1.51	1142	1128
6.01	1505	1505		2.38	1280	1248
8.88	1690	1661		3.57	1455	1399
12.8	1856	1858		5.24	1677	1594
18.3	2165	2110		7.67	1949	1850
26.4	2450	2442		11.4	2250	2250
LiBr				**LiI**		
***P*(GPa)**	***Tm***			***P*(GPa)**	***Tm***	
	(a)	**(b)**			**(a)**	**(b)**
0	820	820		0	723	723
0.268	885	886		0.184	790	791
0.620	970	967		0.428	877	875
1.08	1076	1065		0.762	982	980
1.70	1212	1187		1.22	1146	1115
2.56	1380	1341		1.88	1350	1291
3.77	1611	1542		2.86	1621	1528
5.54	1883	1807		4.35	1959	1857
8.22	2173	2174		6.80	2320	2339
NaF				**NaCl**		
***P*(GPa)**	***Tm***			***P*(GPa)**	***Tm***	
	(a)	**(b)**			**(a)**	**(b)**
0	1261	1261		0	1074	1074
0.52	1337	1337		0.244	1145	1145
1.18	1431	1426		0.556	1233	1229
2.04	1550	1535		0.960	1374	1330
3.16	1695	1666		1.49	1480	1453
4.64	1874	1825		2.19	1648	1605
6.66	2091	2024		3.16	1858	1796
9.48	2374	2277		4.51	2104	2050
13.5	2607	2608		6.45	2363	2363

NaBr			NaI		
***P*(GPa)**	***Tm***		***P*(GPa)**	***Tm***	
	(a)	**(b)**		**(a)**	**(b)**
0	1028	1028	0	924	924
0.182	1098	1098	0.148	996	990
0.416	1185	1181	0.340	1127	1067
0.720	1295	1280	0.590	1200	1161
1.12	1431	1403	0.928	1344	1279
1.66	1601	1553	1.38	1519	1423
2.41	1811	1746	2.02	1734	1610
3.46	2054	1992	2.91	1784	1852
5.02	2304	2321	4.27	2179	2179

KF			KCl		
***P*(GPa)**	***Tm***		***P*(GPa)**	***Tm***	
	(a)	**(b)**		**(a)**	**(b)**
0	1119	1119	0	1049	1049
0.362	1186	1186	0.195	1111	1111
0.824	1269	1266	0.444	1188	1183
1.42	1373	1362	0.774	1286	1272
2.22	1505	1478	1.21	1408	1380
3.27	1666	1621	1.79	1560	1514
4.72	1864	1802	2.59	1745	1682
6.75	2095	2032	3.72	1962	1897
9.71	2336	2335	5.39	2186	2184

KBr			KI		
***P*(GPa)**	***Tm***		***P*(GPa)**	***Tm***	
	(a)	**(b)**		**(a)**	**(b)**
0	1003	1003	0	959	959
0.176	1061	1062	0.139	1017	1017
0.404	1134	1131	0.319	1090	1086
0.696	1225	1217	0.553	1181	1169
1.09	1341	1320	0.864	1295	1272
1.61	1655	1448	1.29	1437	1398
2.34	1662	1610	1.87	1607	1559
3.37	1872	1817	2.70	1801	1767
4.90	2131	2093	3.95	1984	2046

RbF				**RbCl**		
***P*(GPa)**	***Tm***			***P*(GPa)**	***Tm***	
	(a)	**(b)**			**(a)**	**(b)**
0	1048	1048		0	988	988
0.380	1112	1113		0.206	1049	1018
0.872	1194	1191		0.476	1126	1120
1.52	1297	1285		0.828	1224	1208
2.39	1428	1400		1.30	1347	1316
3.58	1595	1546		1.93	1500	1450
5.26	1794	1731		2.82	1691	1621
7.67	2049	1975		4.10	1821	1844
11.3	2299	2307		6.02	2145	2144
RbBr				**RbI**		
***P*(GPa)**	***Tm***			***P*(GPa)**	***Tm***	
	(a)	**(b)**			**(a)**	**(b)**
0	955	955		0	915	915
0.179	1016	1015		0.124	975	971
0.412	1046	1086		0.284	1050	1038
0.714	1194	1176		0.495	1145	1118
1.12	1322	1279		0.775	1263	1219
1.67	1489	1411		1.16	1412	1341
2.44	1705	1579		1.69	1591	1500
3.53	1977	1796		2.45	1794	1705
5.17	2315	2090		3.60	1981	1981

$$\frac{d\ln T_m}{d\ln V} = -2\left[\gamma - \frac{1}{3}\right] \quad \ldots (5)$$

which gives

$$\frac{T_m}{T_{m_0}} = \left(\frac{V}{V_0}\right)^{-2\left(\gamma-\frac{1}{3}\right)} \left[\left(\frac{\gamma_0}{\gamma}\right)\right]^{2\gamma_0/\lambda_\infty} \quad \ldots (6)$$

Eq. (6) is derived using the volume dependence of the Grüneisen parameter γ [14 – 16] given as follows :

$$\frac{1}{\gamma} = \frac{1}{\gamma_\infty} + \left[\frac{1}{\gamma_0} - \frac{1}{\gamma_\infty}\right]\left[\frac{V}{V_0}\right]^{\lambda_\infty} \quad \ldots (7)$$

Eq. (7) is consistent with the thermodynamic constraints formulated by Stacey and Davis [17].

We note from Table 3 that for each material the melting temperature increases considerably with the increase in pressure. For alkali halides, the melting temperature ranges from 723 K to 1261 K. The application of pressure increases the melting temperature very significantly up to more than twice its value at atmospheric pressure. The results obtained in the present study are useful for investigating thermoelastic properties of materials at high temperatures [18-20].

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References

1. Ubbelohde, A.R., The Molten state of matter, John Willey, New York (1978).
2. Anderson, O.L., Equation of state of solids for geophysics and ceramic science, Oxford University Press, New York (1995).
3. Anderson, O.L., Isaak, D.G., Nelson, V.E., *J. Phys Chem. Solids*, **64**, 2125 (2003).
4. Anderson, O.L., *J. Geophys. Res*., **75**, 2719 (1970).
5. Shanker, J. and Kumar, M., *Phys. Stat Sol*., B **158,** 11 (1990).
6. Errandonea, D., *Phys. Rev*., **363,** 132104 (2001).
7. Bochler, R., Errandonea, D., Ross, M., *High Pressure Res*., **22**, 479 (2002).
8. Errandonea, D., *J. Phys. Condens Matter*, **16**, 8801 (2004).
9. Simon, F.E. and Glatzei, G., *Z. Anorg Allg. Chem*., **178**, 178 (1929).
10. Kraut, E.A., Kennedy, G.C., *Phys. Rev*., **151,** 668 (1966).
11. Ksiazek, K. and Gorecki, T., *High Temp. Matter Proc*., **30,** 293 (1999).
12. Ksiazek, K. and Gorecki T., *High Temperatures – High Pressures*, **32,** 205 (2009).
13. Sunil, K., Anand, K., Sharma, B.S., *Indian J. Pure Appl. Phys*., **51,** 444 (2013).
14. Vijay, A., *Physica*, **B 391**, 157 (2007).
15. Srivastava, S.K., Sinha, P., Verma, N., *High Temperatures – High Pressures*, **40,** 169 (2011).
16. Kushwah, S.S., Tomar, Y.S., Sharma, M.P., *High Temperatures – High Pressures*, **41,** 309 (2012).
17. Stacey, F.D. and Davis, P.M., *Phys. Earth Planet Int*., **142,** 137 (2004).
18. Singh, K.S., *Physica*, **B 407**, 668 (2012).
19. Vidyarthi, P.K., Singh, B.P., *Physica*, **B 410,** 259 (2013).
20. Kumar, S., Sharma, S.K., Pandey, O.P., *High Temperatures – High Pressures*, **44,** 339 (2015).

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