Theoretical Evaluation of Thermal Properties of TiO_2 Anatase and Rutile by using Einstein–Debye Approximation

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In this work, we propose a new approach to accurate calculation of heat capacities at constant volume and pressure of TiO_2 anatase and rutile. The evaluation model is based on the Einstein–Debye approximation which has been extensively used in solid state physics. The application of proposed approach to anatase and rutile titanium dioxide computations results is shown to be well numerically satisfactory. This approach is valid in wide temperature ranges and can be suggested for accurate evaluation of thermal properties of solids. The calculation results are in well agreement with the literature values reported by other studies.

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1. Introduction

The titanium dioxide TiO_2 plays important roles in fundamental studies, such as solar cells, biosensors, photocatalysis and thermoelectric devices [1–7]. Titanium dioxide is found in nature in three forms as anatase, rutile, and brookite polymorphs. Note that anatase has more applications despite is less stable than other states. The accurate evaluation problem of thermodynamic properties in various temperature ranges is extremely important for its application area to the conversion of heat into electric power [1, 2]. In the studies dedicated to investigate the thermal properties of titanium dioxide, the various methods have been applied for the whole range of temperature [6–14]. Especially, in study [1], there are some significant numerical results of the isothermal bulk modules, heat capacities, entropy, thermal expansion coefficient and vibrational Helmholtz free energy for titanium dioxide. Also, the some efficient solution approaches are also given in Refs. [12, 13]. In spite of these progress, an alternative new approach is required for accurate evaluation of thermal properties of anatase and rutile TiO_2.

The Einstein and Debye models separately play an important role in evaluation of thermal properties of solids. The Einstein model convoluted with the Debye approximation is one of the most important ingredients for accurate implementation of the heat capacity of solids [15, 16]. The Einstein–Debye model, where all acoustic waves have the same phase velocity and all optical branches have the same frequency, can be used to approximate both acoustic and optical parts of the phonon spectrum. With this in mind, the authors [15, 16] have obtained the general analytical expression which is dependent both on the Einstein temperature and the on Debye temperature. The application of proposed method for calculation of heat capacities of TiO_2 in wide range of temperature should be evaluation of the n-dimensional integer and noninteger Debye functions rapidly and accurate. A general formula has been established for the Debye functions with the integer and noninteger values of n [17]. By using this method, we can calculate the heat capacities of TiO_2 in wide range of temperature.

In this study, we propose an alternative and basic method for calculation of heat capacities of anatase and rutile TiO_2 based on the Einstein–Debye model. The obtained results are compared with the literature data and calculation results provide good agreement for arbitrary values of temperature. Our results could be used as a theoretical support for experimental studies of TiO_2 such as the study of phonon densities [14] and entropy [18].

2. Definition and analytical expressions

Based on a Debye–Einstein model, formulae for evaluation of heat capacities C_V and C_P can be written as, respectively [15, 16, 19]:

$$C_V(T) = 3N_{\mathrm{A}}k_{\mathrm{B}}M\left(T,\theta_{\mathrm{D}},\theta_{\mathrm{E}}\right), \tag{1}$$

$$C_P(T) = C_V(T)\left(1+\frac{A_0T_m}{T}C_V(T)\right). \tag{2}$$

Here, θ_{D} is the Debye temperature, θ_{E} is the Einstein temperature, k_{B} is the Boltzmann constant, N_{A} is the Avogadro number, T is the absolute temperature, T_m is the melting temperature, $A_0 = 5.1\times10^{-3}$ J^{-1} K mol and the quantity $M\left(T,\theta_{\mathrm{D}},\theta_{\mathrm{E}}\right)$ is determined as

$$M\left(T,\theta_{\mathrm{D}},\theta_{\mathrm{E}}\right) = L_V\left(T,\theta_{\mathrm{D}}\right) + (s-1)A\left(T,\theta_{\mathrm{E}}\right), \tag{3}$$

where $L_V\left(T,\theta_{\mathrm{D}}\right)$ is the isochoric heat function and s is the number of atoms in one crystalline lattice point. The $L_V\left(T,\theta_{\mathrm{D}}\right)$ functions for n-dimensional crystal are defined as [15, 16]:

$$L_V\left(T,\theta_{\mathrm{D}}\right) = n\left(\frac{T}{\theta_{\mathrm{D}}}\right)^n\int_0^{\frac{\theta_{\mathrm{D}}}{T}}\frac{t^{n+1}\,\mathrm{e}^t\,\mathrm{d}t}{(\mathrm{e}^t-1)^2} \tag{4}$$

and the function $A\left(T,\theta_{\mathrm{E}}\right)$ is the Einstein function [15]:

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$$A(T,\theta_{\rm E}) = \left(\frac{\theta_{\rm E}}{T}\right)^2 \frac{{\rm e}^{\frac{\theta_{\rm E}}{T}}}{\left({\rm e}^{\frac{\theta_{\rm E}}{T}}-1\right)^2}. \quad (5)$$

The $L_V\,(T,\theta_{\rm D})$ isochoric heat function is expressed in terms of the n-dimensional integer and non-integer Debye functions as

$$L_V\,(T,\theta_{\rm D}) = (n+1)D_n\left(1,\frac{\theta_{\rm D}}{T}\right) - \frac{\theta_{\rm D}}{T}\frac{n}{{\rm e}^{\frac{\theta_{\rm D}}{T}}-1}, \quad (6)$$

where $D_n(1,x)$ are the n-dimensional Debye functions and generally defined as

$$D_n\,(\beta,{\rm x}) = \frac{n}{x^n}\int\limits_0^x \frac{t^n}{({\rm e}^t-1)^\beta}\,{\rm d}t. \quad (7)$$

Recently, the general analytical formula for the n-dimensional Debye function is given by [17]:

$$D_n(\beta,x) = \frac{n}{x^n}\lim_{N\to\infty}\sum_{i=0}^{N}(-1)^i F_i(-\beta)\frac{\gamma(n+1,(i+\beta)x)}{(i+\beta)^{n+1}}, \quad (8)$$

where N is summation limit and $F_i(-\beta)$ are binomial coefficients defined as [20]:

$$F_m(n) = \frac{1}{m!}\prod_{i=0}^{m-1}(n-i). \quad (9)$$

3. Numerical results and discussion

Based on the Einstein–Debye approximation, we have calculated the heat capacities of anatase and rutile TiO_2 for integer and noninteger values of n. The use of the present method for evaluation shows, in its simplicity, a well accuracy. In Tables I–IV our calculation results obtained from Eqs. (1) and (2) for the integer and non-integer values of n in the range (0.4–3.0) compared with the experimental data in Refs. [7–9, 21] and significant matches have been achieved. It is understood from Tables I–IV that the results are satisfactory with experiment for various values of n.

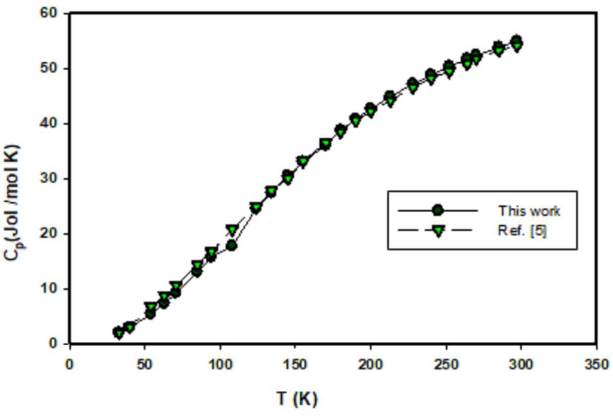

Fig. 1. The temperature dependence of C_P heat capacity of TiO_2 for $\theta_{\rm D} = 760$ K, $\theta_{\rm E} = 670$ K.

TABLE I

The comparative results of $C_V(T)$ heat capacities of rutile titanium dioxide TiO_2 for $\theta_{\rm D} = 760$ K, $\theta_{\rm E} = 673$ K, $T_m = 1843$ K, $N = 200$ (in J mol^{-1} K^{-1})

n	T [K]	Eq. (1)	Exp. [9]
1.2	30	2.235	1.941
1.2	50.5	4.192	5.822
0.9	60	7.361	8.305
0.8	80.4	11.183	12.778
0.4	100	18.261	18.048
0.4	120	22.540	24.118
0.4	140	27.357	28.829
0.4	160	32.247	33.541
0.5	180	36.903	37.694
0.5	200	41.469	41.847
2	220	41.425	45.201
2	239	45.357	47.996
2	250	47.430	49.673
2	270	50.851	52.388
2	290	53.870	54.065
2	310	56.543	56.301
3	330	57.962	57.659
3	350	60.159	59.096
3	370	62.129	60.694
3	400	64.729	62.371

TABLE II

The comparative results of $C_P(T)$ heat capacities of rutile titanium dioxide TiO_2 for $\theta_{\rm D} = 760$ K, $\theta_{\rm E} = 673$ K, $T_m = 1843$ K, $N = 200$ (in J mol^{-1} K^{-1})

n	T [K]	Eq. (2)	Exp. [7, 8]
1.2	32.85	2.098	2.019
1.2	41.55	3.305	3.764
0.9	57.05	7.005	7.483
0.8	69.25	9.482	10.461
0.7	77.96	11.763	12.651
0.6	84.46	13.844	14.35
0.6	91.55	15.116	16.20
0.5	100.5	17.756	18.44
0.3	113.14	20.815	22.05
0.3	123.86	23.132	24.93
0.4	134.66	26.047	27.75
0.4	150.96	30.052	31.82
0.4	161.86	32.693	34.38
0.4	173.15	35.347	36.73
0.5	180.45	37.167	38.33
0.5	192.70	39.917	40.68
0.5	200.68	41.611	42.08
0.5	212.15	43.924	43.99
2	223.65	42.217	45.72
2	235.43	44.653	47.36
2	247.34	46.941	48.89
2	259.30	49.074	50.40
2	265.38	50.098	51.04
2	274.18	51.513	52.02
2	286.57	53.378	53.34
2	298.37	55.028	54.54
2	306.15	56.053	55.28
2	319.26	57.677	56.45
3	332.36	58.234	57.54
3	345.80	59.718	58.20

TABLE III

The comparative results of $C_V(T)$ heat capacities of anatase titanium dioxide TiO_2 for $\theta_D = 740$ K, $\theta_E = 650$ K, $T_m = 1843$ K, $N = 200$ (in J mol^{-1} K^{-1}).

n	T [K]	Eq. (1)	Exp. [21]
1.32	36	2.371	2.260
1.0	50.5	5.604	5.534
0.81	60.4	8.427	8.305
0.6	80	13.444	13.576
0.3	100	18.720	19.406
0.38	120	23.206	24.437
0.4	140	28.082	29.708
0.5	170	35.320	35.937
0.5	190	39.715	40.250
0.8	220	44.929	44.801
1.5	250	48.309	48.795
1.5	280	52.482	52.787
1.5	300	54.626	54.864
1.5	320	56.639	56.062
1.5	340	58.385	58.138
1.5	360	59.907	59.336
1.5	400	62.405	61.891

TABLE IV

The comparative results of $C_P(T)$ heat capacities of anatase titanium dioxide TiO_2 for $\theta_D = 740$ K, $\theta_E = 650$ K, $T_m = 1843$ K, $N = 200$ (in J mol^{-1} K^{-1}).

n	T [K]	Eq. (1)	Exp. [9]
1.6	30.21	1.160	1.109
1.16	45.727	4.051	4.018
1.03	53.62	5.754	5.998
0.89	60.153	7.672	7.732
0.5	96.02	17.419	17875
0.37	115.9	22.409	23.350
0.44	141.12	28.676	29.813
0.44	176.80	37.496	37832
0.44	192.17	40.916	40.799
0.4	204.98	43.338	43.067
0.35	220.41	45.721	45.509
0.35	246.16	49.859	49.197
0.3	259.03	50.796	50.881
0.3	271.96	52.444	52.465
0.3	282.30	53.665	53.546
0.3	290.02	54.526	54.361
0.3	300.37	55.615	55.381
0.3	310.00	56.567	55.280

In the case where integer and noninteger n is applied the results obtained was found to much closer to the experimental data. As seen from the results the main advantages of the analytic approach we analyzed here are, first, that it is valid for an arbitrary temperature range and, in the sense that, it has no insufficiency.

Figure 1 shows temperature dependence of calculated heat capacity of TiO_2 compared with another reported literature values. We can see a satisfactory agreement between the calculated and literature results of anatase and rutile titanium dioxide. As a matter of fact, our formula to compute the n-dimensional Debye functions, occurring in Eq. (6), is faster with respect to other known proposed approaches. The accuracy of analytical method is acceptable and can be suggested for evaluation of other thermal properties of titanium dioxide.

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