



Calculation of the Heat Capacity of Silicon Dioxide

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Keywords

*Silicon Dioxide
Debye Temperature
Heat Capacity
Debye Function*

ABSTRACT

Silicon dioxide, which is the most common quartz phase in nature, is also present in coesite and stishovite polymorphs. In this study, the heat capacity, one of the thermodynamic properties of silicon dioxide, which is widely used in many cosmetic products as well as being used as a raw material for glass, ceramics, semiconductors, and food industry, is discussed. The Debye temperature required to obtain the heat capacity was calculated according to the Veight-Reuss-Hill approach by taking the elastic constants of silicon dioxide, which has a tetragonal structure. The heat capacity corresponds to the amount of heat per unit mass and is one of the most fundamental thermodynamic properties of materials that varies with concentration and temperature. The heat capacity of silicon dioxide has been calculated using the n-dimensional Debye function over the temperature range 60-1000 K. The heat capacity results calculated for SiO₂ are compared with existing experimental and theoretical data. It was observed that the calculated thermal results different temperature was in better agreement with the experimental and theoretical data.

1. Introduction

Silicon dioxide has various allotropic forms in the form of quartz, cristobalite, tridymite, coesite, stishovite and glassy silica (Griscom, 1977; Woodruff, 2001). Both the fused quartz and alpha-quartz crystalline forms of SiO₂ consist of silicon tetrahedrally bonded to four oxygen atoms, with each oxygen atom common to two such SiO₄ tetrahedra (Reilly, 1970). Due to the importance of silicon dioxide in glass production and electronics, the crystal structure of this material has been studied both theoretically and experimentally. Experimental data on the crystal and electronic structure of SiO₂, X-ray absorption and emission spectroscopies, auger electron spectroscopy, low-energy electron-energy-loss spectroscopy, photoelectron spectroscopy, neutron scattering (Fontana, et al., 2005), Raman spectrometry (Hehlen & Simon, 2012), infrared spectrometry (Kirk, 1988), as well as empirical studies potentials were investigated using some computer models prepared using ab initio or reverse (Drabold, 2009) Monte-

Carlo techniques. This inorganic silica glass, which is more resistant to thermal shocks due to its very low thermal expansion coefficient (Xin, et al., 2023) is also widely used in optical, biological, photonic, and optoelectronic fields due to its high optical transparency, outstanding mechanical performance, chemical resistance, and thermal resistance (Axinte, 2011; Camposeo, et al., 2019; Liu, et al., 2021). The SiO₂ is called the main glass-forming material among the four types of oxides used in glass manufacturing. Quartz (Q), Cristobalite (C) and Amorphous SiO₂ (AS) are also of particular importance for magmatic petrology. In this context, these materials are among the favorite materials for making laboratory glass instruments and light bulbs (Axinte, 2011).

Silica (SiO₂), which is commonly found in the form of quartz in the earth's crust, is also included in the components of many ceramic materials (Pabsta, et al., 2016). The natural,

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<http://dx.doi.org/10.56917/ljoas.18>

industrial and theoretical importance of silica requires an accurate knowledge of the thermodynamic properties of different polymorphic forms of silica (Bhattarai & Drabold, 2016). The relationship between the chemical composition and the density of silicate glass melts at temperatures between 1000 and 1400 C° has been statistically studied by Fluegel et al. (2008) and Wang et al. (2001) measured the heat capacity of nanostructured amorphous SiO₂ (na- SiO₂) by adiabatic calorimetric method in the temperature range 9-354 K and reported that the *C_p* values of nanostructured materials are often higher than those of coarse-grained materials. In this study, it is established new analytical formulations for specific heat capacity using the n-dimensional Debye function. As an application, it has been checked our method for heat capacity of SiO₂. The results were compared with those obtained from the literature and are seen to be in good agreement at all temperature values.

2. Materials and Methods

2.1. Debye temperature

The Debye temperature can be expressed in terms of the mean sound velocity. It can be written following form (Anderson, 1963):

$$\theta_D = \frac{h}{k_B} \left[\frac{3n N_A \rho}{4\pi m} \right]^{1/3} v_m \quad (1)$$

where *h* represents the Planck's constant, *k_B* denotes the Boltzmann's constant, *n* signifies the total number of atoms per formula, *N_A* represents the Avogadro number, *ρ* denotes the mass density, *m* represents the molecular weight. The average wave velocity (*v_m*) of the materials can be approximately calculated by using the following Equations (Anderson, 1963)

$$v_m = \left[\frac{1}{3} \left(\frac{2}{v_t^3} + \frac{1}{v_l^3} \right) \right]^{-1/3} \quad (2)$$

$$v_t = \left(\frac{G_H}{\rho} \right)^{1/2} \quad v_l = \left[\left(K_H + \frac{4}{3} G_H \right) / \rho \right]^{1/2} \quad (3)$$

where *v_t* and *v_l* are transverse and longitudinal elastic wave velocity of the polycrystalline materials. We studied the mechanical properties of SiO₂ by calculating the linear elastic constant. Elastic constants for SiO₂ with tetragonal crystal structure; *C₁₁* = *C₂₂* = 91 GPa, *C₃₃* = 86 GPa, *C₄₄* = *C₅₅* = 32 GPa, *C₆₆* = 30 GPa, *C₂₂* = *C₂₁* = -38 GPa and *C₁₃* = *C₂₃* = *C₃₁* = *C₃₂* = 17 GPa. According to the Veight-Reuss-Hill approach (Voight, 1889; Reuss, 1929; Hill, 1952), using the elastic constants for the tetragonal structure, the Bulk and Shear modulus is expressed as follows (Aydin & Simsek, 2011).

$$K_V = \frac{1}{9} [2(C_{11} + C_{12}) + C_{33} + 4C_{13}] \quad (4)$$

$$G_V = \frac{1}{30} [M + 3C_{11} - 3C_{12} + 12C_{44} + 6C_{66}] \quad (5)$$

$$M = C_{11} + C_{12} + 2C_{33} - 4C_{13}$$

$$K_R = \frac{C^2}{M} \quad \text{and} \quad C^2 = (C_{11} + C_{12})C_{33} - 2C_{13}^2.$$

$$G_R = \frac{15}{\{(18 K_V)/C^2 + (6/(C_{11} - C_{12})) + (6/C_{44}) + (3/C_{66})\}} \quad (6)$$

$$K_H = \frac{K_V + K_R}{2} \quad G_H = \frac{G_V + G_R}{2}$$

2.2. Heat Capacity

The Debye function *D_n*(β, *x_D*) is defined by (Bölükdemir, et al., 2018; Eser, et al., 2020; Eser, et al., 2014; Eser & Koç, 2021; Gokbulut, et al., 2021; Guseinov & Mamedov, 2007; Mamedov, et al., 2009)

$$D_n(\beta, x_D) = \frac{n}{x^n} \int_0^x \frac{t^n}{(e^t - 1)^\beta} dt. \quad (7)$$

Heat capacity of materials at constant volume-pressure is given by (Eser et al., 2014; Gokbulut et al., 2021)

$$C_V(T) = 3n_A R B_n(\beta, x) \quad (8)$$

$$C_P(T) = \frac{T_m}{2A_0 T} \left[1 - (1 - 4A_0(T/T_m)C_V(T))^{\frac{1}{2}} \right] \quad (9)$$

In Eq. (8), *n_A* is the number of atoms in the compound, *A₀* = 5.1 × 10⁻³ J⁻¹ K. mol, *T_m* is the melting temperature, *x* = θ/*T*, where, θ is the Debye temperature. If the square root in Eq. (9) expands conveniently into a Binomial series expansion, the Eq. (9) can be written as follows:

$$C_P(T) = \frac{T_m}{2A_0 T} - \lim_{N \rightarrow \infty} \sum_{m=0}^N (-1)^m f_m \left(\frac{1}{2} \right) [2C_V(T)]^m \left(\frac{T_m}{2A_0 T} \right)^{1-m} \quad (10)$$

here the *N* is the upper limit of summation, and *f_m*(*n*) are the binomial coefficients which is defined by (Gradshteyn & Ryzhik, 1980):

$$f_m(n) = \frac{1}{m!} \prod_{i=0}^{m-1} (n - i). \quad (11)$$

In above Eq.(8), *B*(β, *x*) can be expressed by the n-dimensional second kind Debye function defined as:

$$B_n(\beta, x) = \frac{n}{n+1} x_D [D_{n+1}(\beta - 1, x) + D_{n+1}(\beta, x)] \quad (12)$$

where *D_n*(β, *x*) is the n-dimensional Debye function given by Eq.(7).

As can be seen from the above equation Equation (12), the n-dimensional Debye functions are of prime importance in the calculation of the thermodynamic properties of specific heat capacity. We proposed an alternative series formulation for the evaluation of the n-dimensional Debye function given by (Mamedov et al., 2009):

$$D_n(\beta, x_D) = \frac{n}{x_D^n} \lim_{M \rightarrow \infty} \sum_{m=0}^M n! \left\{ 1 - e^{-x_D w} \left(\sum_{k=0}^n \frac{(x_D w)^k}{k!} \right) \right\} w^{-(n+1)} \quad (13)$$

where *w* = *m* + β.

3. Numerical Results and Discussion

For SiO_2 , which has a tetragonal structure, the heat capacity values calculated by taking the Debye temperature calculated according to the Veight-Reuss-Hill approach (Voight, 1889; Reuss, 1929; Hill, 1952) are presented in Table 1 together with

the experimental and theoretical data (Gillet, et al., 1990). Here theoretical values were calculated by Gillet (1990) considering harmonic and anharmonic conditions.

Table 1. Heat capacities $C_p(J mol^{-1}K^{-1})$ of SiO_2 . Experimental and theoretical heat capacity values for SiO_2 are placed for comparison.

		$\theta_D = 523.162 K$			
Eq.(10)		Exp. (Gillet, et al., 1990)	Harmonic (Gillet, et al., 1990)	Anhormanic (Gillet, et al., 1990)	
T(K)	$n = 3$	$n = 2$			
61.1	2,2614	4,8759	5,5336	5,8498	5,3755
122.2	12,0673	16,4472	15,4941	15,4941	15,3360
183.3	22,9228	27,4220	24,5059	24,5059	24,1897
250	32,4444	36,6098	32,4111	32,8854	32,0949
322.2	40,2716	44,0245	39,0514	39,8419	38,8933
372.2	44,6088	48,1063	44,5850	44,7431	43,6364
427.8	48,6886	51,9385	49,1700	49,3281	48,3794
494.4	52,8179	55,8170	53,2806	54,2292	52,3320
561.1	56,3494	59,1389	56,7589	57,5494	55,9684
622.2	59,1920	61,8189	59,6047	60,7115	58,8142
683.3	61,7481	64,2349	62,6087	63,5573	61,0277
750	64,2832	66,6382	64,5059	65,9289	63,3992
816.7	66,6082	68,8490	67,5099	68,7747	65,4545
872.2	68,4137	70,5708	69,8814	70,9881	67,5099
938.9	70,4567	72,5243	72,2530	73,6759	70,1976
1000	72,2267	74,2216	75,4150	75,7312	71,9368

The comparison of the existing experimental heat capacity values for SiO_2 with the heat capacity values obtained in this study is shown in Figure 1. As seen from Fig. 1, the heat capacity of SiO_2 for $n = 3$ is a better good agreement with experimental data than $n = 2$.

The SiO_2 heat capacity values calculated for different temperature values are compared with the values obtained by Gillet et al. (1990) for harmonic and anharmonic states in Fig. 2. It is seen from Fig. 2 that the heat capacity values obtained

for $n = 3$ are more in line with the theoretical calculations in which an intrinsic anharmonic parameter is considered at high temperatures. At high temperatures, it is seen from Figure 2 that the heat capacity values obtained for $n = 3$ are more compatible with the theoretical calculations in which the anharmonic correction term is considered, and the results obtained for $n = 2$ are more compatible with the harmonic theoretical calculations.

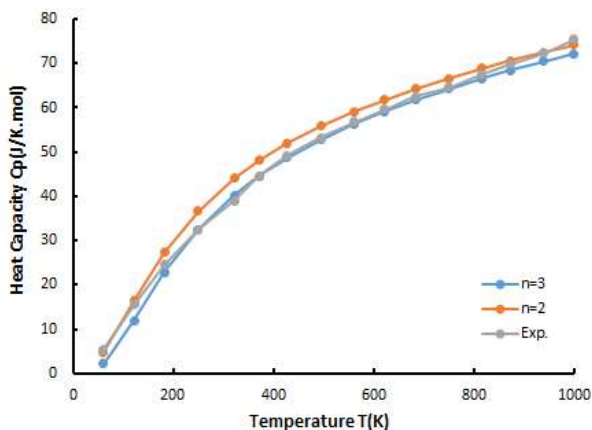


Figure 1. Comparison of the heat capacity values of the SiO_2 for different temperature values with the experimental results.

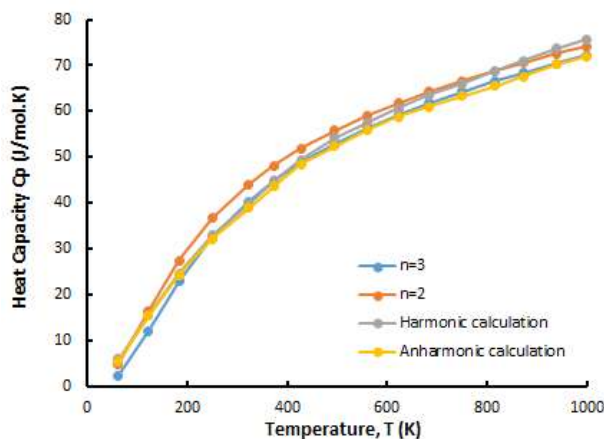


Figure 2. Comparison of the heat capacity values of the SiO_2 for different temperature values with the theoretical results.

4. Conclusion

In this study, the crucial thermophysical property of SiO_2 concerning heat capacity forecasting was calculated using a series formulation derived for the n-dimensional Debye function. It is seen that the obtained results on SiO_2 agreed with the literature data. The results of the present study provide valuable insights into thermophysical properties of SiO_2 , offering useful information for further understanding and analysis. Calculations for $n = 3$ at high temperatures and especially at temperatures above 300 K agree with the anharmonic state, while at low temperatures there is an inconsistency with the anharmonic state. The agreement with the experimental data is evident in the temperature range between 300 – 800 K with the calculations for $n = 3$. From this, it can be concluded that the calculations made in this study better explain the anharmonic structure at 300 K higher temperatures. Calculations for $n = 2$ agree with experimental data at temperatures above 1000 K and below 200 K. Calculations for $n = 2$ are compatible with the harmonic state at temperatures higher than 1000 K. From this, it can be predicted that the harmonic structure can be better explained by the calculations for $n = 2$ at high temperatures.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Cite this article: Gokbulut, M., 2023. Calculation of The Heat Capacity of Silicon Dioxide. Levantine Journal of Applied Sciences, Volume 3(1), 7-11.

<http://dx.doi.org/10.56917/ljoas.18>

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