J Therm Anal Calorim (2012) 107:65–68
DOI 10.1007/s10973-011-1597-3

# Study of size-dependent glass transition and Kauzmann temperature of titanium dioxide nanoparticles

**Shree Mishra · Prafulla K. Jha · Arun Pratap**

29th STAC-ICC Conference Special Chapter


**Abstract** In this article, we have studied the size effect on glass transition and Kauzmann temperature of spherical $TiO_2$ nanoparticles using Arrhenius relation and Lindemann's criteria under their dynamic limit. The melting point of nanoparticles decreases with decrease in size of the nanoparticles. The glass transition temperature and Kauzmann temperature are analyzed through the size effect on the melting temperature. The glass transition and Kauzmann temperatures decrease with the decrease in size of $TiO_2$ nanoparticles.

**Keywords** Nanoparticles · Glass transition temperature · Kauzmann temperature · Melting temperature

## Introduction

Titanium dioxide ($TiO_2$) is a popular material due to many applications arising from its high permittivity, refractive index, efficiency, low cost, chemical inertness, photocatalytic, photostability, and capability of decomposing a wide variety of organics [1, 2]. Controlled synthesis and characterization of nanoparticles is rapidly becoming a very important research area due to their unique shape and size-dependent properties [3, 4]. When the size of material reduces to nanoscale, the quantum confinement effect significantly changes the properties of materials and raises expectations for many novel applications in microelectronics, glasses, and other devices [5–7]. In the recent time there is a considerable interest in the physical properties of $TiO_2$ nanoparticles, due to both the intrinsic properties of titanium oxide compound itself, and the modification obtained because of the nanocrystalline character. $TiO_2$ can be found in a number of crystallographic phases, some of which are stabilized only under high pressure or recovered by decomposition to atmospheric pressure. The size-dependent glass transition is an important parameter for any phase transition process and is related to the thermodynamical properties of material. The understanding of this kind of scientific problem is a challenge particularly in the field of nanotechnology.

Glassy state of substance is considered as metastable state having very long life time and $TiO_2$ nanoparticles is having interesting properties of photo-oxidation response, which has applications in key areas of water splitting and bacterial growth inhibition, therefore kinetics of glass transition temperature and the corresponding thermodynamic transition temperature of $TiO_2$ is of great interest. One can find a few studies related to simulation of $TiO_2$ nanoparticles, in which increase of glass transition temperature of $TiO_2$ nanoparticles with decrease in size is reported [8]. According to Arrhenius theory the, melting temperature $T_m$ of nanoparticles decreases with decreasing size [9], in this article we used unified model which relate glass transition temperature and Kauzmann temperature with melting phenomenon which shows decrease of glass transition temperature and Kauzmann temperature of $TiO_2$ nanoparticles with increase in size, using a simple-empirical method with thermodynamical limit.

S. Mishra · P. K. Jha (✉)
Department of Physics, Bhavnagar University,
Bhavnagar 364022, India
e-mail: pkj@bhavuni.edu; prafullaj@yahoo.com

A. Pratap
Faculty of Technology and Engineering, Applied Physics
Department, The M. S. University of Baroda,
Vadodara 390001, India

## Methodology and computation

According to Lindemann's criterion a crystal melts when root mean square value of amplitude thermal vibration ($\sigma$) of atoms or molecules reaches a critical function of inter-atomic distance at particular temperature and expressed as [9],

$$\sigma^2(r,T) = F(r)T, \tag{1}$$

where, $F(r)$ is a size-dependent function. At melting temperature, the size-dependent critical function can be expressed as [9],

$$\frac{F(r)}{F(\infty)} = \frac{\{\sigma^2(r, T_m(r)/h^2)\}}{\{\sigma^2(\infty, T_m(\infty)/h^2)\}}\left[\frac{T_m(\infty)}{T_m(r)}\right] = \frac{T_m(\infty)}{T_m(r)}. \tag{2}$$

In terms of Lindemann's criterion [10], we can write melting temperature as,

$$\frac{T_m(r)}{T_m(\infty)} = \frac{\sigma^2(\infty)}{\sigma^2(r)} = \exp\left\{\frac{-(\alpha-1)}{\left[\left(\frac{r}{r_0}\right)-1\right]}\right\}, \tag{3}$$

where $\alpha = S_{vib}(r)/(3R) + 1 \cdot S_{vib}(\infty)$ is the bulk melting entropy and essential contribution on the overall bulk melting entropy,$r_0 = c_1(3-d)h$, where $d$ is extended for different dimension with $d = 0$ for nanosphere, $d = 1$ for nanowires, and $d = 2$ for thin films, $c_1$ is added as an additional condition for different surface states which in the case of nanocrystals is equal to unity [11]. Since glasses as solid is having same structural feature of short range order as crystal, so they should have same vibrational characteristics at melting temperature of $T_g$ and $T_m$. But as glass transition temperature is considered as second order phase transition, it can be achieved by substituting $C_{pm}(\infty)$ instead of $S_{vib}(r)$ in Eq. 3, which is heat capacity difference between the liquid and the crystal at $T_m(\infty)$, and as a phenomenological observation, it is assumed that $\sigma_g^2(\infty) = \sigma^2(\infty)$ and $\sigma_g^2(r) = \sigma^2(r)$ where g denotes glass transition temperature $T_g$. Finally the Eq. 3 takes the following form [9],

$$\frac{T_g(r)}{T_g(\infty)} = \frac{\sigma_g^2(\infty)}{\sigma_g^2(r)} = \exp\left\{\frac{-(\alpha-1)}{\left[\left(\frac{r}{r_0}\right)-1\right]}\right\}. \tag{4}$$

The Gibbs free energy change for crystallization of an undercooled liquid ($\Delta G$) is an important parameter in the nucleation theory and also in predicting the glass forming ability of alloys, but exact temperature dependence of $\Delta G$ value can be estimated only if Kauzmann temperature $T_K$ is known [12]. As Kauzmann temperature cannot be measured experimentally, here we used relation between melting temperature and Kauzmann temperature and calculated Kauzmann temperature of $TiO_2$ nanoparticle theoretically using Kauzmann theory [13]. According to Kauzmann theory, $T_K$ is called the entropy crisis temperature where liquid and its crystalline counterpart have the same entropy [12],

$$S_m(T_K) = S_l(T_K) - S_s, \tag{5}$$

where $S_m(T)$ denotes temperature dependent melting entropy, and the subscript m, l, and s represent the melting, liquid, and crystal transition, respectively. Equation 5 can be realized using temperature-dependent Gibbs free energy difference between liquid and the crystal in bulk. It can be obtained experimentally as follows [13]:

$$G_m(T,\infty) = \frac{7TH_m(\infty)[T_m(\infty)-T]}{T_m(\infty)[T_m(\infty)+6T]}, \tag{6}$$

where $H_m(\infty)$ is bulk melting enthalpy. This implies that $G_m(T, \infty)$ reaches its maximum at $T_K$. Namely, $dG_m(t, \infty)/dT = T_K = 0$ [13],

$$T_K(r) = \left[\frac{\sqrt{7}-1}{6}\right]T_m(r), \tag{7}$$

where $T_m(r)$ is melting temperature based on Lindemann criterion which we have calculated using Eq. 3.

## Results and discussion

This article reports the calculated results on the size-dependant glass transition temperature $T_g$ and Kauzmann temperature $T_K$ of $TiO_2$ nanoparticles using Eqs. 3 and 7, respectively. Figure 1 presents the variation of glass transition $T_g$ with the size for $TiO_2$ nanoparticles. This figure reveals that the glass transition temperature of $TiO_2$ nanoparticles increases as size of the $TiO_2$ nanoparticles increases and approaches to bulk glass transition temperature point, of 1300 K at around 15 nm. The glass transition temperature variation with size is similar to the size variation of melting temperature of $TiO_2$ nanoparticles [11] and some other metal nanoparticles [14, 15]. There is a rapid drop of the glass transition temperature below 15 nm in contrast to the melting temperature which shows the rapid drop at 5 nm. This is due to the fact that the size of nanoparticles decreases, surface to volume ratio increases, so there are more number of surface atoms which are loosely bound and are responsible for the decrease in glass transition of $TiO_2$ nanoparticles. However, the process of glass transition is slower than melting transition temperature in $TiO_2$ nanoparticles. The rapid drop of $T_g$ at 15 nm may be due to the Lindemann criteria. According to Lindemann criteria, root mean square value of amplitude thermal vibration of atoms in $TiO_2$ nanoparticles reaches critical value at 15 nm, so there is sharp observed. It is important to mention that the molecular dynamics

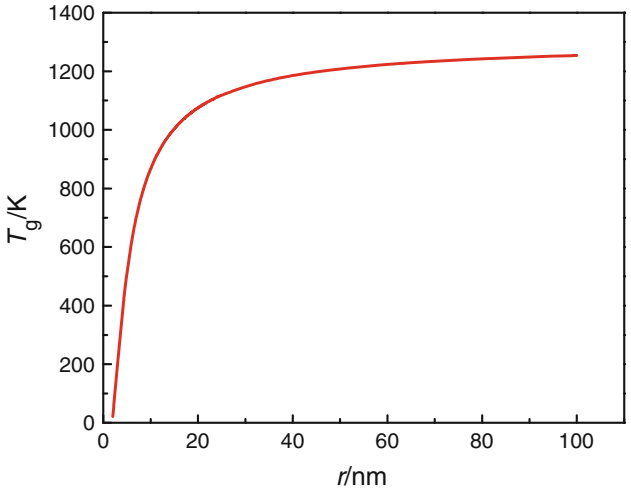


**Fig. 1** $T_g(r, T)$ function of $TiO_2$ as a function of size. The related parameter in Eq. 7 are $h = 0.3768$ nm [19], $T_g(\infty) = 1300$ K [8], and $C_p(\infty) = 39.48$ J mol$^{-1}$K$^{-1}$ [21]

simulation of Hoang [16] predicts that the glass transition temperature increases with the decrease in size of the $TiO_2$ nanoparticles which seems unphysical as well as contradicts the general nature of glass transition temperature. The glass forming ability of any material can be known if the Gibbs free energy of crystallization is known which is normally obtained using the knowledge of Kauzmann's temperature. The glass forming ability of $TiO_2$ nanoparticles have been calculated using reduced glass transition temperature (Turnbull's condition) for the $TiO_2$ nanoparticles of different sizes and presented in Table 1. The Table 1 reveals quite good agreement with Turnbull prediction [17, 18] (i.e., if this ratio comes 2/3 then liquid can be easily undercooled at low cooling rate into glassy state) for smaller size nanoparticles from 5 to 10 nm but as size of nanoparticles increases this ratio increases gradually. This predicts that glass forming ability of nanoparticles is more than the bulk $TiO_2$. The relation of glass forming ability of $TiO_2$ nanoparticles with melting and glass transition temperature is based on the short range order in glasses. Since glasses as solid is having short range order, so they have same vibrational characteristics of melting temperature of $T_m$ and glass transition temperature $T_g$.

Figure 2 presents the Kauzmann temperature of $TiO_2$ nanoparticles, calculated using Eq. 7. This figure depicts that the Kauzmann temperature of $TiO_2$ nanoparticles depends on size of nanoparticles similar to the melting and glass transition temperature. However, the Kauzmann temperature, $T_K$ lies below the glass transition $T_g$. A remarkable feature is observed that the Kauzmann temperature has lower values below the nanoparticles of 4 nm size are due to the thermodynamical limit. To obtain a statistical limit, any size effect due to thermal fluctuation above 3% (i.e., below 4 nm) are not addressed in this study and other method such as density functional theoretical calculation can be considered for such small nanostructures.

**Table 1** Glass transition temperature, melting temperature, and reduced glass transition temperature of $TiO_2$ nanoparticles for different sizes

| $r$ (nm) | $T_g$/K | $T_m$/K | $T_{rg} = T_g/T_m$ |
|---|---|---|---|
| 5 | 515.411 | 987.649 | 0.522 |
| 6 | 623.252 | 1027.948 | 0.606 |
| 7 | 706.413 | 1055.411 | 0.6693 |
| 8 | 772.001 | 1075.322 | 0.717 |
| 9 | 824.854 | 1090.417 | 0.756 |
| 10 | 868.264 | 1102.254 | 0.787 |

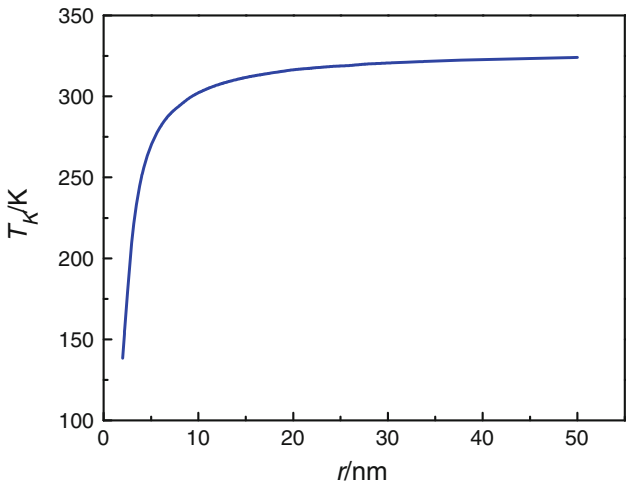


**Fig. 2** $T_K(r, T)$ functions of $TiO_2$ denoted as a *solid line* in terms of Eq. 3. The related parameters in Eq. 3 are $h = 0.3768$ nm [19], $T_m(\infty) = 1200$ K, and $S_m(\infty) = 126.60$ J mol$^{-1}$K$^{-1}$ [20]

## Conclusions

We have calculated the glass transition and Kauzmann temperature for $TiO_2$ nanoparticles using Arrhenius theory and Lindemann criterion. We have shown, contrary to the commonly accepted opinion, that glass transition temperature of $TiO_2$ nanoparticles decreases with increasing size or glass transition temperature of $TiO_2$ nanoparticle is independent of size. We have also shown that Kauzmann temperature of $TiO_2$ also depends on size of nanoparticles. There is a rapid drop of glass transition temperature below 15 nm. This is, however, a higher value than the melting temperature where the rapid drop takes place much below this size. The Kauzmann temperature lies below the glass transition temperature for the $TiO_2$ nanoparticles for all sizes consistent with the observation.

**Acknowledgements** The authors acknowledge financial support from Department of Science and Technology, New Delhi and University Grants Commission, New Delhi.

## References

1. Ito A, Shinkai M, Honda H, Kobayashi T. Medical application of functionalized magnetic nanoparticles. J Biosci Bioeng. 2005;100:1–11.
2. Rout CS, Raju AR, Govindraj A, Rao CNR. Hydrogen sensors based on ZnO nanoparticles. Solid State Commun. 2006;138: 136–8.
3. Wang X, Song J, Liu J, Wang ZL. Direct-current nanogenerator driven by ultrasonic waves. Science. 2007;316:102–5.
4. Martinez CJ, Hockey B, Montgomery CB, Semancik S. Porous tin oxide nanostructured microspheres for sensor applications. Langmuir. 2005;21:7937–44.
5. Tjong SC, Chen H. Nanocrystalline materials and coatings. Mater Sci Eng R. 2004;45:1–8.
6. Meyers MA, Mishra A, Benson DJ. Mechanical properties of nanocrystalline materials. Prog Mater Sci. 2006;51:427–556.
7. Timp G, editor. Nanotechnology. New York: AIP Press, Springer; 1999.
8. Hoang VV. The glass transition and thermodynamics of liquid and amorphous $TiO_2$ nanoparticles. Nanotechnology. 2008;19: 105706–19.
9. Jiang Q, Yang CC. Size effect on the phase stability of nanostructures. Curr Nanosci. 2008;4:179–200.
10. Shi FG. Size dependent thermal vibrations and melting in nanocrystals. J Mater Res. 1994;9:1307–13.
11. Mishra S, Gupta SK, Jha PK, Pratap A. Study of dimension dependent diffusion coefficient of titanium dioxide nanoparticles. Mater Chem Phys. 2010;123:791–4.
12. Dhurandhar H, Lad K, Pratap A, Dey GK. Gibbs free energy difference in bulk metallic glass forming alloys. Defect Diffus Forum. 2008;279:91–6.
13. Ao ZM, Zheng WT, Jiang Q. Size effects on the Kauzmann temperature and related thermodynamic parameters of Ag nanoparticles. Nanotechnology. 2007;18:255706–12.
14. Guisbiers G, Buchaillot L. Size and shape effects on creep and diffusion at the nanoscale. Nanotechnology. 2008;19:435701–7.
15. Gupta SK, Talati M, Jha PK. Shape and size dependent melting point temperature of nanoparticles. Mater Sci Forum. 2008;570:132–7.
16. Hoang VV. Pressure-induced structural transition in amorphous $TiO_2$ nanoparticles and in the bulk via molecular dynamics simulation. J Phys D Appl Phys. 2007;40:7454–61.
17. Qi WH. Size effect on melting temperature of nanosolids. Phys B. 2005;368:46–50.
18. Turnbull D, Fisher JC. Rate of nucleation in condensed systems. J Chem Phys. 1949;17:71–3.
19. Li G, Boerio-Goater J, Woodfield B, Fand Li L. Evidence of linear lattice expansion and covalency enhancement in rutile $TiO_2$ nanocrystals. Appl Phys Lett. 2004;85:2059–63.
20. Cooke DJ, Parker SC, Osguthorpe DJ. Calculating the vibrational thermodynamic properties of bulk oxides using lattice dynamics and molecular dynamics. Phys Rev B. 2003;67:134306–9.
21. Smith JS, Stevens R, Liu S, Li G, Navrotsky A, Boerio-Goates J, Woodfield BF. Heat capacities and thermodynamic functions of $TiO_2$ anatase and rutile: analysis of phase stability. Am Miner. 2009;94:236–43.