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Study of size-dependent glass transition and Kauzmann temperatures of tin dioxide nanoparticles

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Abstract The size and shape effects on melting, glass transition, and Kauzmann temperatures of SnO_2 nanoparticles using Lindemann's criterion have been studied. The melting temperature of SnO_2 nanoparticles decreases as the size of the particle decreases. As the particle size increases, melting temperature increases and approaches to the melting temperature 1,903 K of bulk irrespective of the shape. The glass transition and Kauzmann temperatures are analyzed through the size effect on the melting temperature. The glass transition and Kauzmann temperatures decrease with the decrease in size of SnO_2 nanoparticles.

Keywords Glass transition temperature · Melting temperature · Kauzmann temperature · SnO_2 · Nanoparticles

Introduction

Nanostructured oxides have received considerable attention due to their unique properties and application prospects in novel nanodevices. A reduction in particle size to nanometer scale results in various interesting properties compared to their bulk properties [1–3]. The nanosized tin dioxide has great potential in wide applications due to its higher surface to volume ratio. It is evident that the important parameters of nanostructured materials such as size, crystallinity, purity, morphology, and surface condition of the particles depend on the processing method and synthesizing parameters. In accomplishing manipulation of the nanostructured tin dioxide, a variety of strategies have been employed, such as chemical precipitation [4], microwave technique [5], gel combustion route [6], sol–gel [7], solvothermal [8], hydrothermal [9], sonochemical [10], mechano-chemical [11], and solid-state [12] methods.

The melting of nanocrystals has received considerable attention since Takagi in 1954 [13] experimentally demonstrated that ultrafine metallic nanocrystals melt below their corresponding bulk melting temperature $T_m(\infty)$ with ∞ denoting the bulk. In the present paper, we focus on the effects of size and shape on melting, glass transition, and Kauzmann temperatures of SnO_2 nanoparticles. 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. In this article, we used unified model which relates glass transition and Kauzmann temperatures with melting phenomenon which shows decrease of glass transition and Kauzmann temperatures of SnO_2 nanoparticles with decrease in size, using a simple empirical method with thermodynamical limit [14].

Methodology and computation

As per Lindemann's criterion, expression for size-dependent function of amplitude thermal vibration is given by [15]

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$$\sigma^2(r,T) = F(r)T. \quad (1)$$

It states that a crystal melts when root mean square displacement (msd) of the atoms in crystal (σ^2) reaches a critical function of inter-atomic distance at particular temperature. Here, $F(r)$ is a size-dependent function. At melting temperature, the size-dependent critical function can be expressed as [15]

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

If size dependence of h is neglected, melting temperature based on Lindemann's criteria can be written as [16],

$$\frac{T_m(r)}{T_m(\infty)} = \frac{\sigma^2(\infty)}{\sigma^2(r)} = \exp\left\{\frac{-(\alpha-1)}{\left(\frac{r}{r_0}\right)-1}\right\}. \quad (3)$$

where $\alpha = 2S_{vib}(r)/(3R) + 1$.

$S_{vib}(\infty)$ is the melting entropy of corresponding bulk system and R is the ideal gas constant. If r_0 is the radius at which all atoms of the particle are located on its surface, it should be dimension dependent for low-dimensional crystals and can be calculated by $r_0 = c_1(3-d)h$. c_1 is the additional factor for different surface states and equals to 1 in the case of nanocrystals. The parameter d depends upon different dimensions, i.e., $d = 0$ for nanocrystals, $d = 1$ for nanowires, and $d = 2$ for thin films. In general, for nanoparticles and nanowires, r has a usual meaning of radius and for a thin film, r denotes its half thickness. Let h be the atomic diameter, r_0 is given by (a) $r_0 = 3\ h$ for $d = 0$ since $4\pi r_0^2 h = 4\pi r_0^3/3$; (b) $r_0 = 2\ h$ for $d = 1$ since $2\pi r_0 h = \pi r_0^2$; and (c) $r_0 = h$ for $d = 2$ since $2h = 2r_0$ [17].

Glasses are solids having structural feature of short-range order like crystal, so they should have same vibrational characteristics at melting temperature of T_g and T_m. But glass transition temperature is considered as second-order phase transition, so it can be obtained 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, Eq. 3 can be expressed in the following form [15]:

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

The change in Gibbs free energy for crystallization of an undercooled liquid (ΔG) is an important parameter to predict the glass forming ability of alloys but estimation of exact temperature dependence of ΔG value is possible only if Kauzmann temperature T_K is known [18]. Here, we have used relation between melting and Kauzmann temperatures to calculate Kauzmann temperature of SnO_2 nanoparticles theoretically using Kauzmann theory because Kauzmann temperature cannot be measured experimentally [19]. According to Kauzmann theory, T_K is called entropy crisis temperature where liquid and their crystalline counterparts have the same entropy [18],

$$S_m(T) = S_l(T) - S_s(T). \quad (5)$$

where $S_m(T)$ denotes temperature-dependent melting entropy, and the subscripts m, l, and s represent the melting, liquid, and crystal transitions, 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 [19]:

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

where $H_m(\infty)$ is bulk melting enthalpy. This indicates $G_m(T,\infty)$ reaches its maximum at T_K. Therefore, $dG_m(T,\infty)/dT = T_K = 0$ [19] and Eq. 6 provides

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

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

Results and discussion

The calculated results on the size-dependent glass transition temperature T_g and Kauzmann temperature T_K of SnO_2 nanoparticles using Eqs. 3 and 7, respectively, have been discussed in this article. Figure 1 shows the variation of melting temperature T_m with the size for SnO_2 nanoparticles. Figure 2 presents the variation of glass transition T_g with the size for SnO_2 nanoparticles. This figure reveals that the glass transition temperature of SnO_2 nanoparticles increases as size of the SnO_2 nanoparticles increases and approaches to bulk glass transition temperature point, of 758 K at around 40 nm. We have found similarity between size variations of glass transition and melting temperatures of SnO_2 nanoparticles [20] and some other metal nanoparticles [21, 22]. There is a rapid drop of the glass transition temperature below 10 nm which is similar to the variation of melting temperature. This is due to the fact that as the size of nanoparticles decreases, surface area to volume ratio increases. Because of that, there are more number of surface atoms which are more reactive and loosely bound. These atoms are responsible for the decrease in glass transition of SnO_2 nanoparticles. The

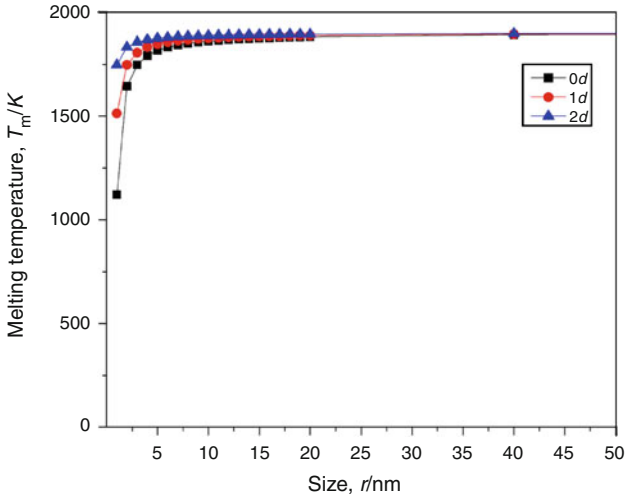

Fig. 1 $T_m(r, T)$ function of SnO_2 as a function of size. The related parameters in Eq. 3 are $h = 0.2057$ nm [24], $T_m(\infty) = 1{,}903$ K, and $C_p(\infty) = 4.098$ J mol^{-1} K^{-1} [24]

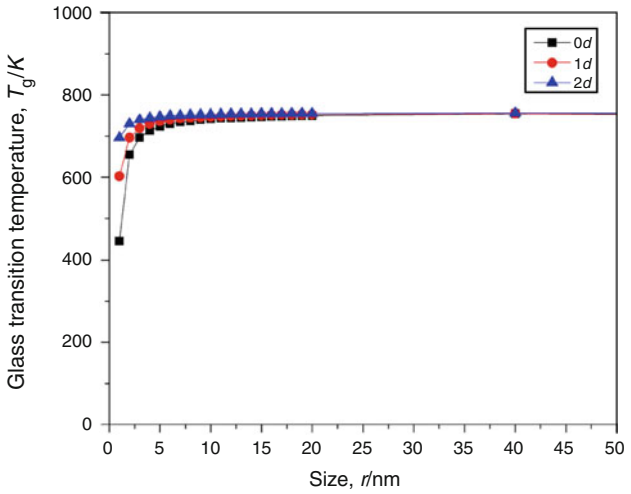

Fig. 2 $T_g(r, T)$ function of SnO_2 as a function of size. The related parameters in Eq. 4 are $h = 0.2057$ nm [24], $T_g(\infty) = 758$ K [25], and $C_p(\infty) = 4.098$ J mol^{-1} K^{-1} [24]

rapid drop of T_g at 10 nm may be due to the Lindemann's criterion. Based on that, root mean square value of amplitude thermal vibration of atoms in SnO_2 nanoparticles reaches critical value at 10 nm, a sharp drop is observed. It is important to mention that the molecular dynamics simulation of Hoang [23] 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. If Kauzmann temperature is known, Gibbs free energy of crystallization can be estimated and from that glass forming ability of any material can be obtained.

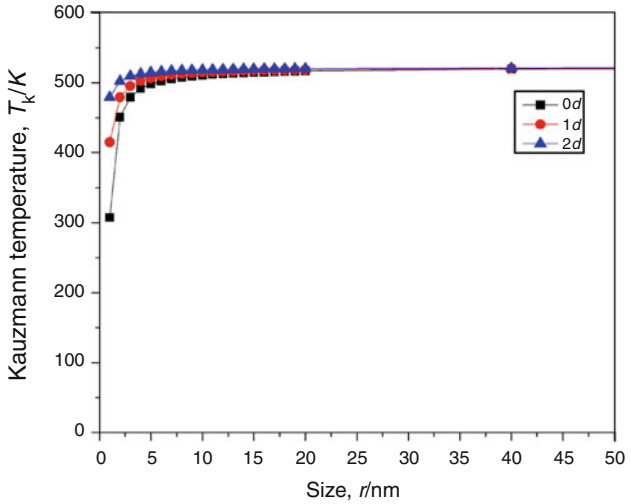

Fig. 3 $T_K(r, T)$ function of SnO_2 denoted as a *solid line* in terms of Eq. 7. The related parameter is $T_m(\infty) = 1{,}903$ K

Figure 3 presents the Kauzmann temperature of SnO_2 nanoparticles, calculated using Eq. 7. This figure shows that the Kauzmann temperature of SnO_2 nanoparticles depends on size of nanoparticles similar to the melting and glass transition temperatures. However, the Kauzmann temperature, T_K lies below the glass transition T_g [14].

Conclusions

The present paper reports the calculated size-dependent melting temperature of SnO_2 nanostructures in 0*d*, 1*d*, and 2*d*. The behavior of melting temperature is similar for the relatively larger nanoparticles irrespective of their dimensions but there is a considerable difference for nanoparticles below the range of 5 nm. We have calculated the glass transition and Kauzmann temperatures for SnO_2 nanoparticles using Arrhenius theory and Lindemann criterion. It can be seen that there is a rapid drop of glass transition temperature below 10 nm. This is, however, a similar value as observed in case of the melting temperature T_m. The Kauzmann temperature lies below the glass transition temperature for the SnO_2 nanoparticles for all sizes consistent with the observation.

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