Modelling for the Study of Thermoelastic Properties of Nanoparticles

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In the present work, we have proposed a very simple model to predict the thermoelastic properties of nanosolid, nanowire and nanofilm of Selenium, Copper, Silver, Lead, Tin, Zinc and Nickel elements with the variation of temperature at their different sizes. In our study, it is observed that compression (V/V0) increases with temperature in nanospheres, nanowires and nanofilms of the considered elements. The rate of increment is the highest for nanosolid. We also found that the compression decreases with an increase in size. The thermal expansivity and bulk modulus vary with shape and size and shows significant deviation in thermoelastic parameters.

Introduction

The compression behavior of nanomaterials under the effect of high temperature has also been a very enthusiastic topic for the researchers. Because this behavior makes nanomaterials different from its bulk counterparts. The size-dependent thermal expansion of nanomaterials is of current interest. The crystallite size and the lattice parameter evaluation are key factors to describe the size-dependent properties of nanomaterials. The reduction in crystalline size is followed by a variation of lattice parameters. The surface to volume ratio in nanomaterials is different from that of their bulk material. Because of the surface effects, nanomaterials possess more rich metastable structures than their bulk form [**1-4**]. It was found that with a reduction of grain size, the linear thermal expansion coefficient increases significantly, thus volume thermal expansion coefficient increases. A linear increase in lattice parameters and thermal expansion as a function of temperature indicates a linear lattice thermal expansion.

Although many researchers have attempted to study the effect of temperature on the compression of nanomaterials of different shapes and sizes, but the experimental observations are still lacking. Since, the size of nanomaterials affects the thermal properties of nanomaterials significantly thus, in the present work we have developed a model to predict the variation of compression of nanomaterials with temperature at different sizes of nanomaterials.

Method of analysis

The pressure dependent equation of state formulated by Gupta and Goyal [**5**] at room temperature T_0 is as given below:

$$P(V,T_0) = K_0\left(\frac{V_0}{V}-1\right) + K_0\left(\frac{K_0^{'}-1}{2}\right)\left(\frac{V_0}{V}-1\right)^2 \qquad (1)$$

where V_0 is the initial volume at room temperature, V/V_0 is the volume compression, K_0 is the bulk modulus at zero pressure and $K_0^{'}$ is its first pressure derivative.

From above equation, we get following expression as suggested by Goyal and Gupta [**6**]

$$\left(\frac{V}{V_0}\right)^{-1} = 1 + \frac{\left\{K_0^2 + 2K_0 P(V,T_0)(K_0^{'}-1)\right\}^{1/2} - K_0}{K_0(K_0^{'}-1)} \qquad (2)$$

For thermal effect, thermal pressure term P_{th} is incorporated to total pressure acting on the solid at temperature T as suggested by Anderson [**7**]

$$P(V,T_0) = P(V,T_0) + P_{th} \qquad (3)$$

Where $$P_{th} = \alpha_0 K_0 (T-T_0) \qquad (4)$$

where α_0 is volume thermal expansion coefficient at room temperature T_0

Using above equations, we get

$$\left(\frac{V}{V_0}\right)^{-1} = 1 + \frac{\left\{K_0^2 + 2K_0 (P-P_{Th})(K_0^{'}-1)\right\}^{1/2} - K_0}{K_0(K_0^{'}-1)} \qquad (5)$$

Again $$\left(\frac{V}{V_0}\right)^{-1} = 1 + \frac{\left\{K_0^2 + 2K_0 \{P-\alpha_0 B_0 (T-T_0)\}(K_0^{'}-1)\right\}^{1/2} - K_0}{K_0(K_0^{'}-1)} \qquad (6)$$

For nanomaterials, α_0 is replaced by α_N at room temperature T_0.

At zero pressure, the isobaric EoS for nanomaterials in obtained as

$$\left(\frac{V}{V_0}\right)^{-1} = 1 - \frac{1 - \left\{1 - 2\alpha_N (T-T_0)(K_0^{'}-1)\right\}^{1/2}}{(K_0^{'}-1)} \qquad (7)$$

where α_N is the thermal expansion coefficient of nanomaterials. It is formulated by Kumar and Kumar [**8**]

$$\alpha_N = \alpha_B\left(1 - \frac{N}{2n}\right)^{-1} \qquad (8)$$

Qi [**9**] suggested the method to find *N/2n* for different shapes of nanomaterials and the expressions of *N/2n* have been tabulated in **Table 1**.

Table 1. In terms of the size the values of N/2n for different types of nanostructured materials [9].

S. No.	Nanomaterials	N/2n
1.	Spherical nanosolids	2d/D
2.	Nanowires	4d/3l
3.	Nanofilms	2d/3h

where *D* is the diameter of a spherical nanosolid, *d* is the diameter of the atom, *l* is the length of nanowire and *h* is the height of nanofilm and α_B is the thermal expansion coefficient of bulk counterpart.

Results and discussion

The model proposed by us requires the input values of atomic diameter d and volume thermal expansion coefficient α_0 for the bulk materials. In the present work, B_0 is approximated to 4 and the size of the nanomaterial is considered to be less than 100 nm.

The input data required for the calculations are listed in **Table 2**.

To test our model, we have taken seven metallic nanoparticles as mentioned in the **Table 2**. Very few experimental data are available for the variation of compression of nanomaterials with temperature. Out of all seven samples the experimental is available only for the Se sample [**17**]. We have tested our model for Se nanoparticles at different sizes. The variation of compression (V/V_0) of Se nanoparticles with the temperature at 13 nm, 19 nm, 21 nm and 24 nm has been shown in **Fig. 1 – Fig. 4** along with the available experimental data. From these graphs it is quite evident that our computed results are in good agreement with the experimental results. This agreement proves the validity of our model.

Table 2. Input parameters for some nanostructured materials [10-16].

S. No.	Nano-particles	d(nm)	α_N (*10^{-5} K^{-1})	B_0
1.	Cu	0.2556	4.9	4
2.	Se	0.437	9.45	4
3.	Ag	0.144	5.83	4
4.	Pb	0.390	8.7	4
5.	Sn	0.372	2.2	4
6.	Zn	0.495	0.54	4
7.	Ni	0.248	3.3	4

At the nano level, materials show very interesting physical properties with the variation of shape and size [**18-20**]. With the exciting results obtained with our model, we have applied it to all seven samples mentioned in **Table 2**. We have computed the compression of nano solids, nanowires and nanofilms of copper (Cu) at the varying temperature for their dimensions of 15 nm, 25 nm and 50 nm. The graphs showing the variation of compression of nano solids, nanowires and nanofilms with the temperature at different sizes are shown in the Fig. 5(a) – Fig. 5(c). From these plots it is clear that compression of nanoparticles varies linearly with temperature at the different sizes of the particle. This can be explained with the fundamental concept that the thermal expansion of materials is proportional to the temperature. Interestingly it is observed that the compression of nanosolids is more for the smaller nanoparticles than the bigger one. This variation can be explained on the basis of the fundamental concept of the large surface to volume ratio in the case of nanomaterials. As the size of nanoparticles decreases, a greater number of atoms lie at the surface of nanoparticles. With the increase in the temperature the surface atoms of smaller nanoparticles will be more active to show much compression than the nanoparticles of larger size at the same temperature. The same is also reported in the experimental observed [**19**] shown in the **Fig. 1 - Fig. 4**. Thus, we observe that our model is in good agreement with experimental results and we can apply this model for the prediction of the behavior of nanomaterials at the extreme temperature conditions.

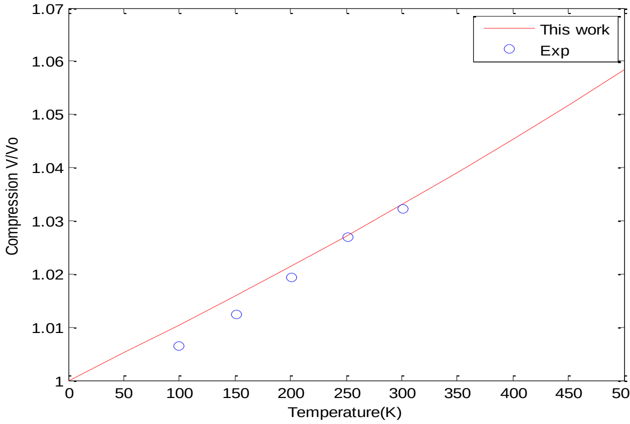

Fig. 1. Compression behavior of Se(13nm) nanosolid for varying temperature.

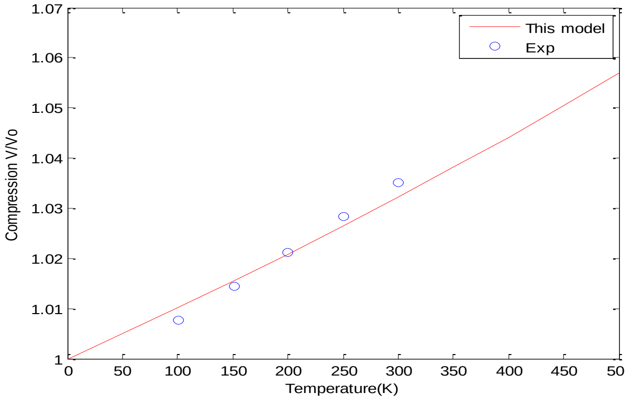

Fig. 2. Compression behavior of Se(19nm) nanosolid with varying temperature.

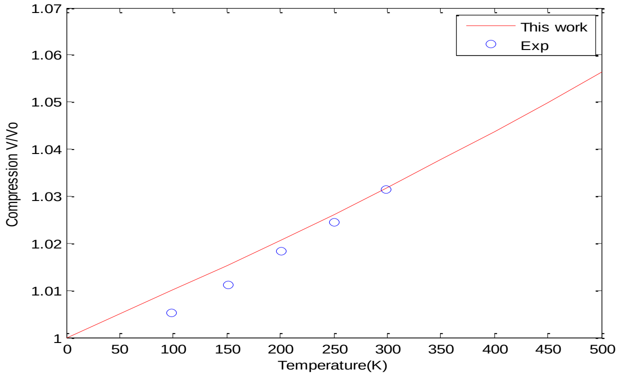

Fig. 3. Compression behavior of Se(21nm) nanosolid with varying temperature.

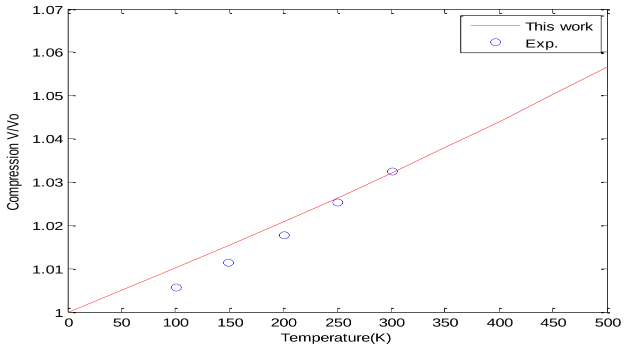

Fig. 4. Compression behavior of Se(24nm) nanosolid with varying temperature.

We have also applied our model to the nanowire and nanofilms of the same material for the prediction of its compression behavior at different temperatures for the different sizes as shown in **Fig. 5(b)** and **Fig. 5(c)**. Almost the same behavior has been observed in the case of nanowire and nanofilms as it was for nano solids except the rate of variation in the compression. The rate of variation of compression with temperature in case of nano solid is more than the nanowire while the nanowires have more compression rate than nanofilms. It can again be explained on the basis of number of atoms are lying on the surface of the nanomaterials of different shape. It is obvious that that maximum number of atoms will lie at the surface of nanosphere (nanosolids). In case of nanowire there will be again a greater number of atoms at the surface than the corresponding nanofilm. Thus, the rate of compression of different shape will vary accordingly.

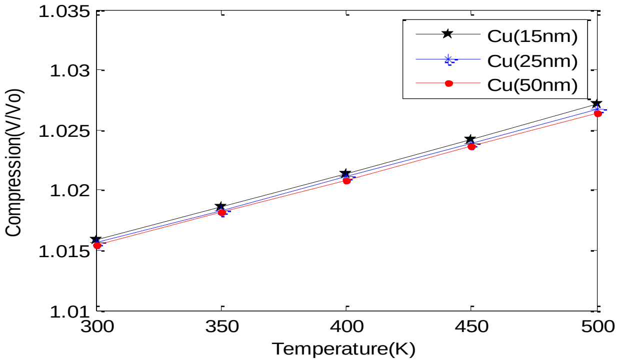

Fig. 5(a). Compression behavior of Cu nanosolid with varying temperature and size.

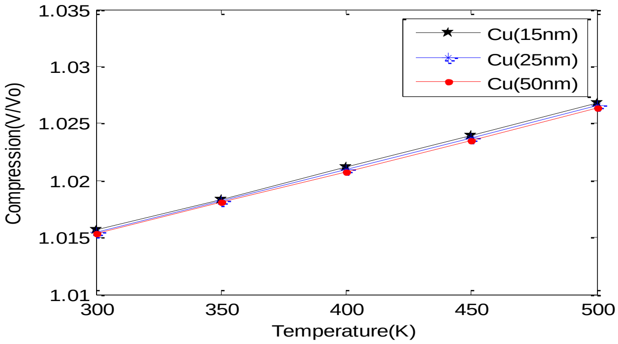

Fig. 5(b). Compression behavior of Cu nanowire with varying temperature and size

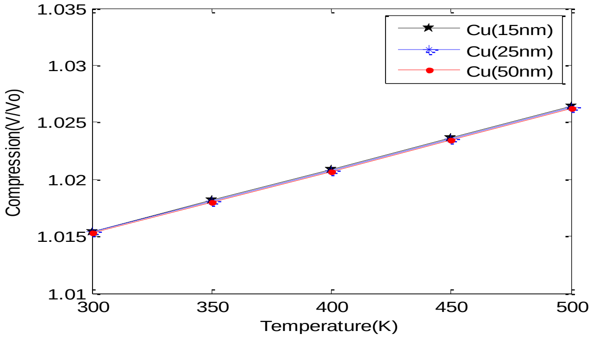

Fig. 5(c). Compression behavior of Cu nanofilm with varying temperature and size.

We have also applied our model for nano solid, nanowire and nanofilms of Selenium (Se), Silver (Ag), Lead (Pb), Tin (Sn), Zinc (Zn) and Nickel (Ni) metallic nanoparticles to study the effect of temperature on volume thermal expansion as well as their shape and size. The variation of their thermal compression with temperature at different sizes has been shown in the **Fig. 6(a) – Fig. 6(c), Fig. 7(a) - Fig. 7(c), Fig. 8(a) - Fig. 8(c), Fig. 9(a) - Fig. (c), Fig. 10(a) - Fig. 10(c)** and **Fig. 11(a) - Fig. 11(c)** respectively. In all these graphs we observed almost the same variation as it is observed and explained in the case of copper (Cu). Similar to copper (Cu) we also observe the same compression behavior of nanofilms as well as nanosolids and nanowires in case of other samples. From the above-mentioned figures it is noticed that the compression behavior of nano solids is comparatively less than that of nanowires. It is also clear that the dependency of size on compressibility (V/V0) is more for nanosolids than that of nanowires and nanofilms.

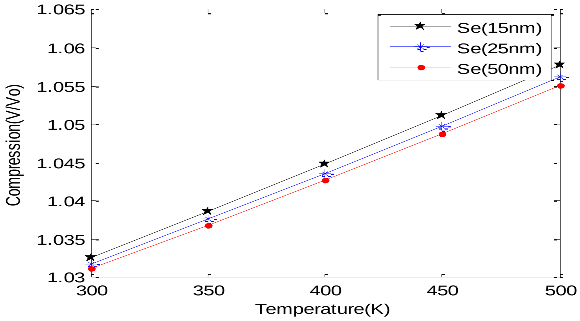

Fig. 6(a). Compression behavior of Se nanosolid with varying temperature and size.

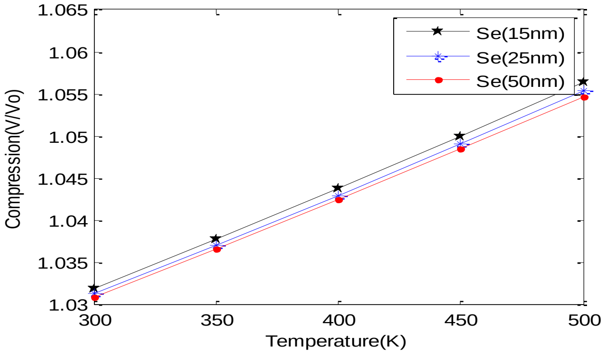

Fig. 6(b). Compression behavior of Se nanowire with varying temperature and size.

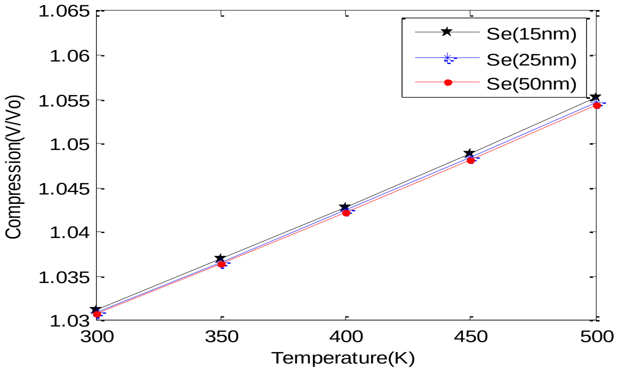

Fig. 6(c). Compression behavior of Se nanofilms with varying temperature and size.

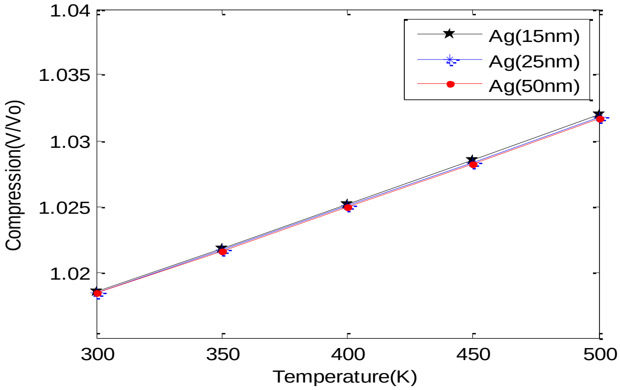

Fig. 7(a). Compression behavior of Ag nanosolid with varying temperature and size.

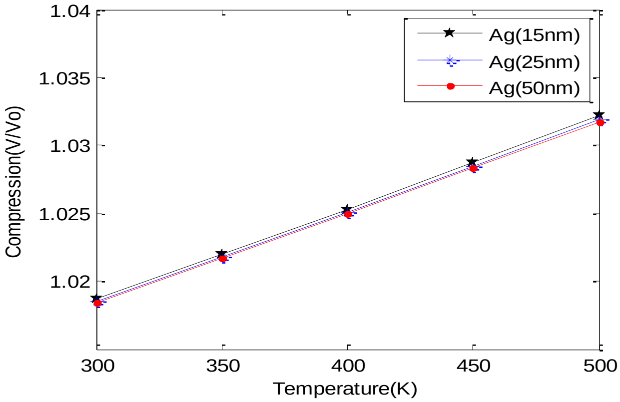

Fig. 7(b). Compression behavior of Ag nanowire with varying temperature and size.

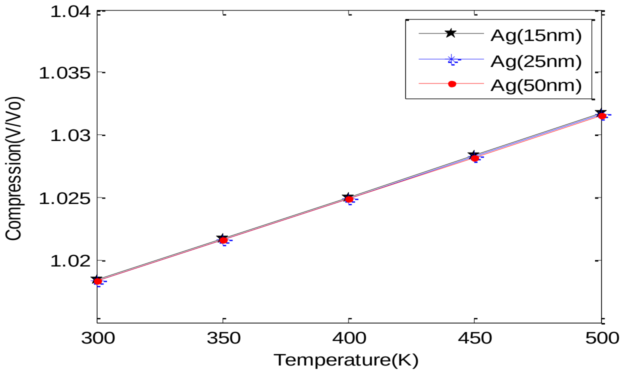

Fig. 7(c). Compression behavior of Ag nanofilm with varying temperature and size.

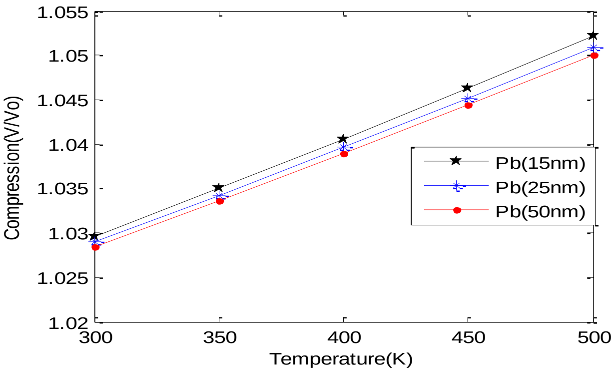

Fig. 8(a). Compression behavior of Pb nanosolid with varying size and temperature.

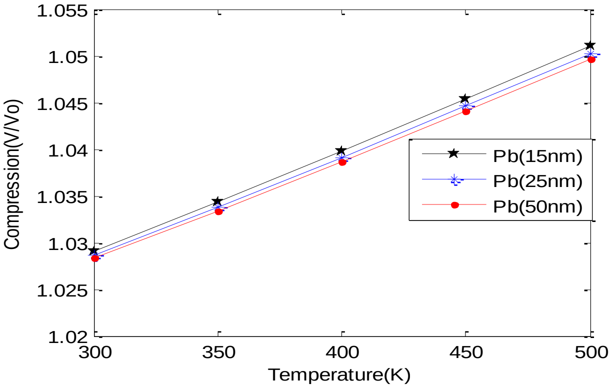

Fig. 8(b). Compression behavior of Pb nanowire with varying temperature and size.

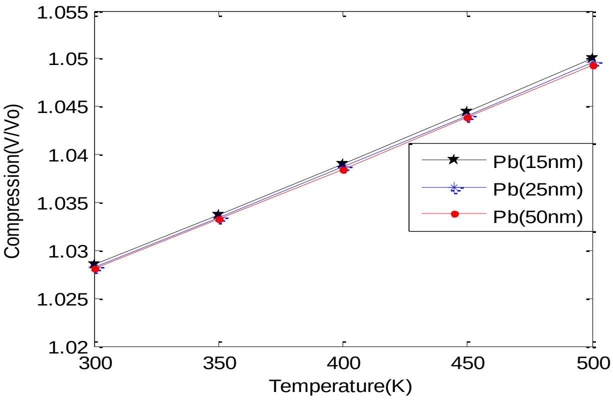

Fig. 8(c). Compression behavior of Pb nanofilm with varying temperature and size.

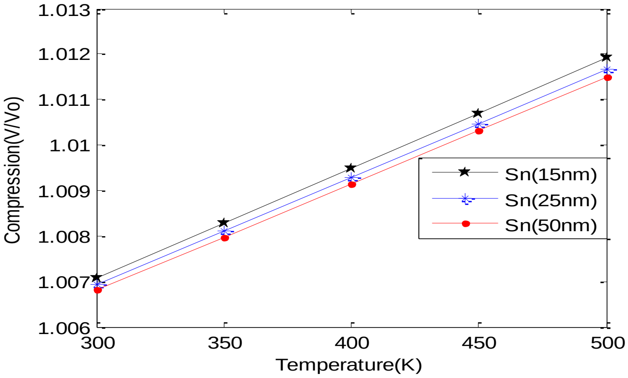

Fig. 9(a). Compression behavior of Sn nanosolid with varying temperature and size.

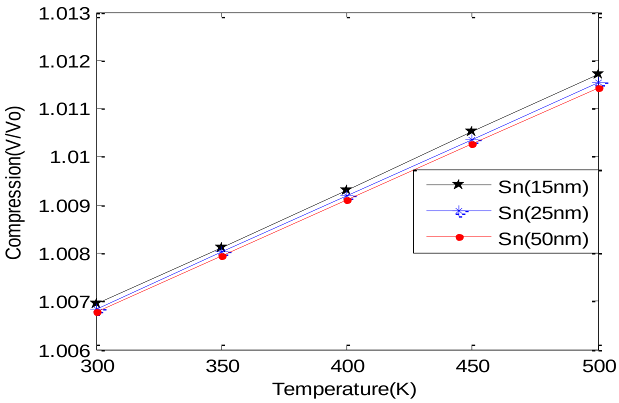

Fig. 9(b). Compression behavior of Sn nanowire with varying temperature and size.

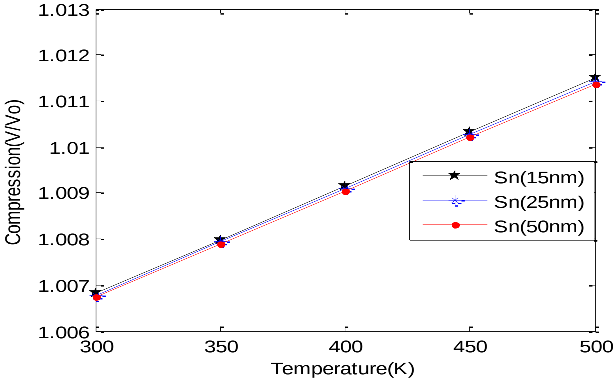

Fig. 9(c). Compression behavior of Sn nanofilm with varying temperature and size.

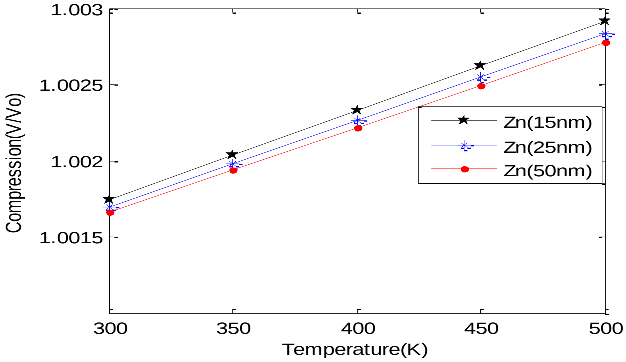

Fig. 10(a). Compression behavior of Zn nanosolid with varying temperature and size.

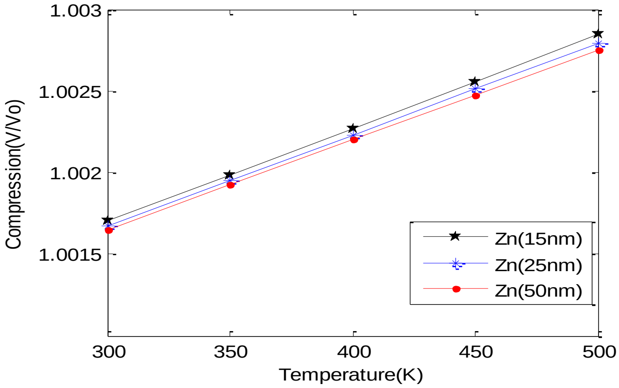

Fig. 10(b). Compression behavior of Zn nanowire with varying temperature and size.

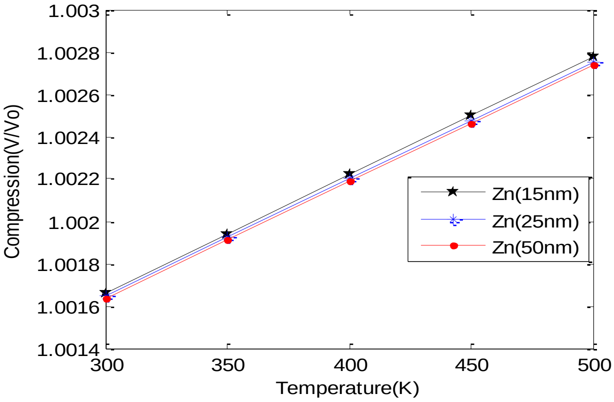

Fig. 10(c). Compression behavior of Zn nanofilm with varying temperature and size.

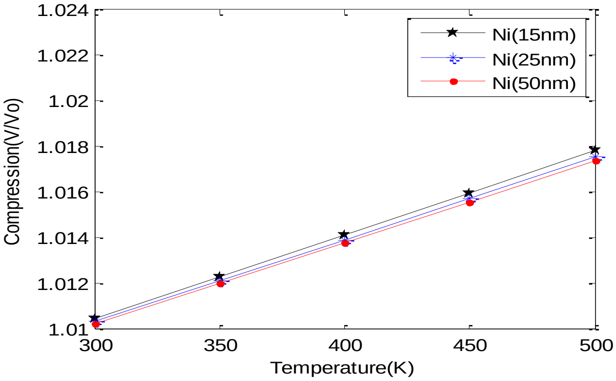

Fig. 11(a). Compression behavior of Ni nanosolid with varying temperature and size.

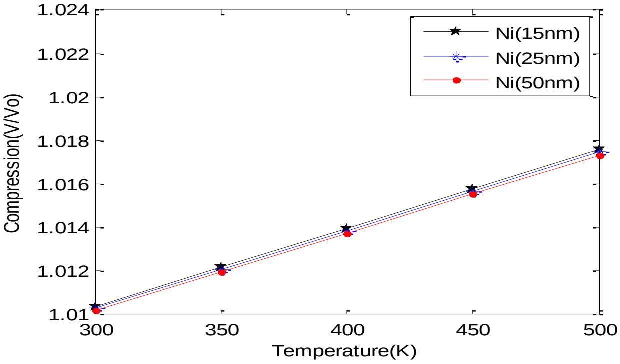

Fig. 11(b). Compression behavior of Ni nanowire with varying temperature and size.

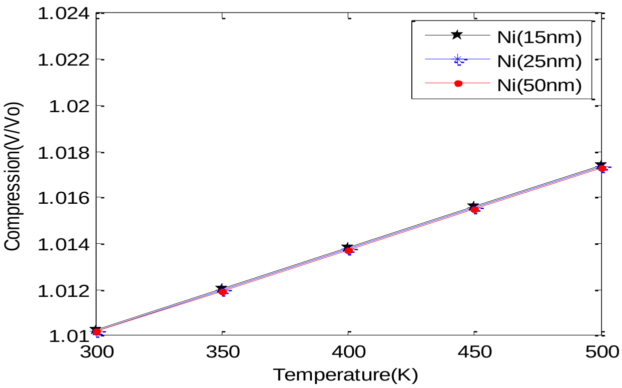

Fig. 11(c). Compression behavior of Ni nanofilm with varying temperature and size.

More ever it is observed that an increase in volume compressibility is more significant in spherical nanosolid for particle size less than 30 nm. it can be stated that the particle size and shape affect the thermal properties of nanomaterials, especially when the size is less than 30 nm. This is probably due to the increase in surface area to volume ratio with a decrease in the size of nanosolids. From the above-mentioned figures, it is also evident that the particles of size less than 30 nm, shape parameter plays a dominant role in the thermoelastic properties of nanomaterials. It is observed that the thermal expansivity and bulk modulus vary with shape (spherical, nanowires, nanofilms) as well as with size (< 30nm) and show significant deviation in thermoelastic parameters. However, for a particle having their sizes more than 30 nm, the effect of shape is not much significant. Due to which the variation in volume expansion and bulk modulus corresponding to different shapes having their sizes more than 30 nm is negligible. All these observations are in good agreement with the available experimental data.

On the basis of these results we conclude that the present model can be used as the universal model for the prediction of the effect of temperature on volume thermal expansion at different shapes and sizes of metallic nanoparticles.

Conclusion

Increase in compression (V/V_0) with the increase in temperature in spherical nanomaterials, nanowires and nanofilms of the considered nanomaterials is due to the thermal expansion in the crystal lattice with increase in temperature, as in general, materials expand on heating. It is found that the compression decreases with an increase in size. It is also observed that with an increase in temperature, the compression also increases. The rate of increment is higher particularly in the case of nano solids. But for bigger sizes the rate of increase in compression is lower than that of smaller sizes of nanomaterials. It is noticed from the figures plotted for different samples that the bulk modulus increases with increase in temperature of nanomaterials forming nanosolids, nanowires and nanofilms. This rate of increment observed maximum in spherical nanoparticles. For particles of size less than 30 nm, the shape parameter plays a dominant role. It is observed that thermal expansivity and bulk modulus vary with shape (spherical, nanowires, nanofilms) and size (< 30nm), which shows significant deviation in thermoelastic parameters. However, for a particle whose size is more than 30 nm, the effect of shape is not much significant as the variation in volume expansion and bulk modulus corresponding to different shapes is negligible. These computed results based on our model have good agreement with the available experimental data.

Thus, we can conclude that when we incorporated the concepts suggested by Qi [**9**] into model proposed by Goyal *et. al.*, [**6**] and Kumar *et. al.*, [**8**], we found better results. Also we tried to study the effect of temperature on volume compression as well as the effect of size and the type of nanomaterials and finally, we can say that our model can be used as a universal model for the prediction of thermoelastic properties of nanomaterials up to the level of desired temperature.

Conflicts of interest

There are no conflicts to declare.

Keywords

Thermoelastic property, compression, thermal expansivity, nanostructure.

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