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Size Dependent Thermo Elastic Properties of Nano Lead Sulfide (PbS) under High Pressure

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ABSTRACT

Present paper reports a theoretical study to investigate the compressional behavior of nano PbS($V/V_0, B_T, \alpha_r$) under high pressure by using different equations of state. The pressure dependence of these parameters for three nano PbS particles of different sizes (2.6nm, 5.4nm and 8.8nm), have been calculated by using B-M EOS, m L-J EOS and S-K EOS. Obtained results are compared with available experimental data. This comparison reveals the validity of using the well-known EOSs of bulk materials such as B-M EOS and m L-J EOS further to S-K EOS which was used for studying nano materials. The effect of particle's size, under high pressure, have been investigated in present work. The overall results in this work let us put question mark about S-K EOS.

Keywords: Nano PbS, EOS, High Pressure, Galina, Nano Materials.

INTRODUCTION

Nano materials science is one of the important fields of nano technology and is based on presenting nano materials related to nano technology. Nano materials science is concerned with the study of materials and morphology of nano scale dimensions, especially those that have properties arise as a result of their nano dimension. The "nano scale" is defined as being smaller than 0.1 μm in at least one dimension, although this term is sometimes used for materials with dimension smaller than 1 μm.

One of the features of nano technology is the large ratio of surface area to volume in most nano materials which leads to many new quantum effects, such as, the "quantum volume effect" where the electronic properties of solids change significantly in the size of nano particle. Despite these effects are not effective when moving from macro dimension to micro dimension. But it becomes apparent upon reaching the nano scale. (Jalal *et al*., 2021)

Therefore, the new mechanical properties of nano materials are one of the topics under investigation in nano mechanics. In general, nano technology is the creation and application of scientific and engineering ideas for the purpose of understanding and producing new materials and devices. These products generally contribute to expanding the use of physical properties associated with nano materials. (Buzen *et al.*, 2016)

In recent, years (Sharma and Kumar, 2016), the science and technology of high pressure has evolved from a highly specialized field to abroad field in the physical science. One of the most important technological developments is the integration of nano technology with micro samples under high pressure. As well as that high pressure allows new entrance to understanding the damage of softening and distortion in nano particles. These examples open new horizons for high pressure researches. (Mao *et al.,* 2016).

Lead sulfide (galena) is an inorganic compound with the chemical formula PbS. It has a crystal structure similar to NaCl. It is the main ore for lead and is toxic if heated to the point of dissolution, as it produces lead and sulfur oxide. PbS has uses in infra-red sensors. In optoelectronics, and in properties of slip treatments to enrich thermal conductivity and regulate friction parameters. (Azo network, 2013).

Whereas the use of EOSs in theoretical high-pressure studies allows the use of mathematical interpolation and mathematical extrapolation, to obtained data under extreme high pressure that cannot be accessed experimentally. The use of EOSs in high pressure studies is a promising way for further advancement in scientific research. (Joshi and Senger, 2013).

THEORETICAL DETAILS

An equation of state is a formula that the thermodynamic variables pressure, temperature, volume and number of atoms relate to one another (Chandra, 2008).

It is known that there is a universal equation of state for ideal gas which was formulated as

$$PV = nRT \qquad \text{..........................(1)}$$

where P is pressure, V is volume, n is number of moles in gas, R: general gas constant =8.3145J/mole. K. (Young, 2007)

In present work, pressure dependence of volume compression (V/V_0), isothermal bulk modulus (B_T) and relative isothermal expansion coefficient ($\alpha(P)/\alpha_0$) for nano PbS have been studied, using the following equations of states.

1- Birch-Murnaghan Equation of State (Birch, 1947).

The well-known and widely used EOS is the Birch- Murnaghan equation of state, which is based on the assumption that isothermal bulk modulus B is a linear function of pressure at any temperature; that is

$$P_{B-M} = \frac{3}{2} B_0 \{ (\frac{V}{V_0})^{-7/3} - (\frac{V}{V_0})^{-5/3} \} \times [1 - \frac{3}{4}(B_0^{'} - 4)\{(\frac{V}{V_0})^{-2/3} - 1\}] \quad ...... (2)$$

P_{B-M}: the lower subscript refers to Birch-Murnaghan EOS, P is the pressure.
$V_{0:}$ is the volume at pressure (p=0).
V: is the volume at a high-pressure p.
B_0: is the bulk modulus at pressure (p=0).
B'_0 is the first pressure derivative of bulk modulus.

2- Modified General Lennard-Jones Equation of State (m GLJ EOS) (Jiuxun, 2005).

GL-J EOS is not volume analytic as the exponents contained in the potential function take arbitrary values.

On making the exponent satisfying a relationship, GL-J EOS become volume analytic with two parameters (m GLJ EOS) and is expressed as:

$$P_{mL-J} = \frac{B_0}{n}\left(\frac{V}{V_0}\right)^{-n}\left[\left(\frac{V}{V_0}\right)^{-n} - 1\right] \quad ……………………….. (3)$$

where: $P_{m\,L\text{-}J}$**:** the lower subscript points to modified L-J EOS, P is the pressure.
n= (1/3) $B_0^{'}$.

3- Singh and Kao Equation of State (Singh and Kao, 2013)

(Singh *et al.*, 2012) derived a simple EOS and used it to study the volume expansion of some nano materials under high pressure. Only two input parameters, namely, the bulk modulus and its first pressure derivative are required for calculations.

(Singh and Kao, 2013) reproduced an equation using the theory of Mie-Grüneisen EOS, which defines pressure as:

$$P = -\frac{\partial U}{\partial V} + P_{th} \quad …………………………………………… (4)$$

Where P_{th} is the thermal pressure, U is the lattice potential energy?

$$P_{S-K} = B_0\left[1 - \frac{V}{V_0}\right] + \left[\frac{B_0(B_0^{'}+1)}{2}\right]\left(1 - \frac{V}{V_0}\right)^2 \quad ………………………….. (5)$$

P_{S-K} : the lower subscript points to Singh and Kao

Isothermal Bulk Modulus (B_T):

The bulk modulus (B_0) is the ratio between the stress resulting from hydrostatic pressure to the volumetric strain and it is measured in units (GPa) and is given by the following relationship:

$$B_T = -\frac{P}{\Delta V / V} \quad …………………………. (6)$$

or $$B_T = -V\frac{\partial P}{\partial V} \quad ………………………………. (7)$$

where V : the original volume, ΔV : change in the volume, P : the pressure.

Bulk modulus is also defined that it is a measure of material resistance to regular compression when an external pressure on that material (Abdulateef and Al-Shiekh, 2020).

Evaluation of Isothermal Bulk Modulus (B_T) using Different EOSs

The mathematical form for isothermal bulk modulus (B_T) under high pressure from different EOSs have been evaluated on the basis of bulk modulus definition as given in equation (7) then:

(i) On using B-M EOS as given in eq. (2) one has

$$B_{T(B-M)} = -V\left(\frac{\partial P_{B-M}}{\partial V}\right)_T \qquad \text{....... (8)}$$

while

$$\frac{dP_{B-M}}{dV} = \frac{3}{2}B_0\left[-\frac{7}{3}\left(\frac{V^{-7/3-1}}{V_0^{-7/3}}\right) - \frac{9}{4}(B_0'-4)\left(\frac{V^{-3-1}}{V_0^{-3}}\right) + \frac{7}{2}(B_0'-4)\left(\frac{V^{-7/3-1}}{V_0^{-7/3}}\right) + \frac{5}{3}\left(\frac{V^{-5/3-1}}{V_0^{-5/3}}\right) - \frac{5}{4}(B_0'-4)\left(\frac{V^{-5/3-1}}{V_0-^{5/3}}\right)\right] \qquad \text{......(9)}$$

and

$$B_{T(B-M)} = -V\left(\frac{dP_{B-M}}{dV}\right)_T = \frac{3}{2}B_0\left[\frac{7}{3}\eta^{-7/3} + \frac{9}{4}(B_0' - 4)\eta^{-3} - \frac{7}{2}(B_0' - 4)\eta^{-7/3} - \frac{5}{3}\eta^{-5/3} + \frac{5}{4}(B_0' - 4)\eta^{-5/3}\right] \qquad \text{....... (10)}$$

Where

$\eta = V / V_0$.

similarly

(ii) Using modified Lennard Jones EOS: as given in eq. (3)

$$B_{T(m\,L-J)} = -V\left(\frac{dP_{m\,L-J}}{dV}\right) \qquad \text{....... (11)}$$

and

$$B_{T(m\,L-J)} = B_0\left(\frac{V}{V_0}\right)^{-n}\left[2\left(\frac{V}{V_0}\right)^{-n} - 1\right] \qquad \text{....... (12)}$$

where $n = (1/3)B_0'$

Furthermore

(iii)On using Singh and Kao EOS as given in eq. (5)

$$B_{T(S-K)} = -V\left(\frac{dP_{S-K}}{dV}\right) \qquad \text{....... (13)}$$

and

$$B_{T(S-K)} = B_0\left(\frac{V}{V_0}\right)\left[1 + \left(1 + B_0'\right)\left(1 - \frac{V}{V_0}\right)\right] \qquad \text{....... (14)}$$

Many researches (Al-Shiekh and Issa, 2020; Chandra and Kholiya, 2016) found that the variation of the B_T under the influence of high pressure is a promising approach to the formulation of a universal EOS for solid materials.

The Relative Isothermal Expansion Coefficient α/α$_0$:

Thermal expansion is a property of a material, in which there is a tendency for an increase in volume due to an increase in temperature. The degree of thermal expansion of a substance divided by the change in temperature is called the coefficient of thermal expansion, and it is a characteristic of materials, as each material has its own coefficient of thermal expansion.

The coefficient of thermal expansion describes how the volume of something changes with the change in temperature. Specifically, it measures the relative change in volume when a temperature changes of one degree under constant pressure.
(Paul *et al.*, 2008)

$$\alpha_r = \frac{\alpha(P)}{\alpha_0} = \frac{B_0}{B}$$

,where

α_r *is relative isothermal volume* exp*ansion ceofficien t*

$\alpha(P)$ *is isothermal* exp*ansion coefficien t at pressure*(P)

α_0 *is the isothermal* exp*ansion coefficien t at atmosphere pressure*$(p = 0)$

In present paper relative isothermal expansion coefficient has been evaluated under high pressure by using different EOSs as following:

(i) U sing B-M EOS

Substituting eq. (10) into eq. (15) gives

$$(\alpha_r)_{B-M} = \frac{2}{3}\left[\frac{7}{3}\eta^{-7/3} - \frac{5}{3}\eta^{-5/3} - \frac{9}{4}(B_0^{'} - 4)\eta^{-3} + \frac{7}{2}(B_0^{'} - 4)\eta^{-7/3} - \frac{5}{4}(B_0^{'} - 4)\eta^{-5/3}\right]^{-1} \quad \text{……..(16)}$$

Similarly Using modified Lennard Jones EOS (m L-J EOS):

substituting eq. (12) into eq. (15) gives

$$\left(\frac{\alpha(P)}{\alpha_0}\right)_{m\,L-J} = \frac{B_0}{B_{T(m\,L-J)}} \quad \text{…………………………… (17)}$$

$$(\alpha_r) = \frac{B_0}{B_0(V/V_0)^{-4/3}[2(V/V_0)^{-4/3} - 1]} \quad \text{………………………………… (18)}$$

$$(\alpha_r)_{m\,L-J} == \eta^{4/3} \times [2\eta^{-4/3} - 1]^{-1} \quad \text{………………………………… (19)}$$

where $\eta = V/V_0$

(ii) Using Singh and Kao EOS:

$$\frac{\alpha(P)}{\alpha_0} = \frac{B_0}{B_{T(S-K)}} \quad \text{……………………………….. (20)}$$

Substituting eq. (14) into eq. (15) gives

$$(\alpha_r)_{S-K} = \left[(V/V_0)[1 + (1 + B_0^{'})(1 - V/V_0)\right]^{-1} \quad \text{………………………… (21)}$$

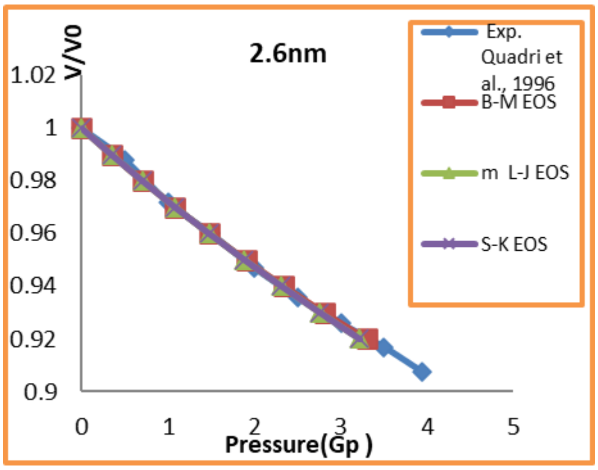
CALCULATIONS AND RESULTS

1. Calculations of nano PbS isotherm under high pressure using different EOSs

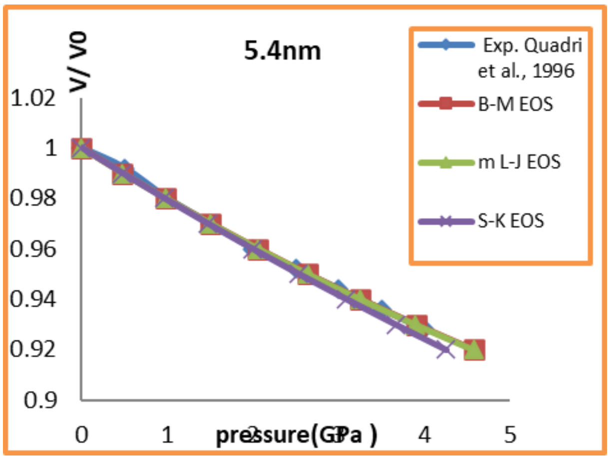
(Table 1) shows the values of B_0 and $B_0^{'}$ for different sizes of PbS nano particles. Substituting B_0 and $B_0^{'}$ values from Table 1 into equations 2,3 and 5 respectively. Figs. (1 a,b,c) show PbS nano particles isotherm under high pressure for (2.6, 5.4 and 8.8) nm respectively.

Table 1: B_0 and $B_0^{'}$ values for different sizes of PbS nano particles.

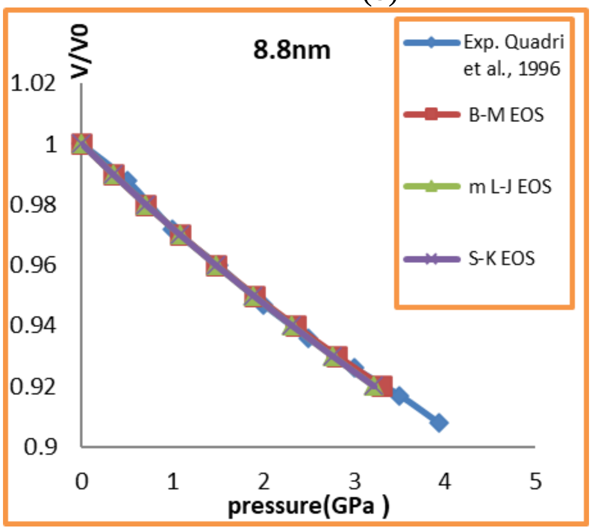
Parameter	Size in nm			Ref.
	2.6	5.4	8.8	
B_0	33.5	46.51	75	Chandra and Kholiya, 2013
$B_0^{'}$	4.0	4.0	4.0	



(a)



(b)



(c)

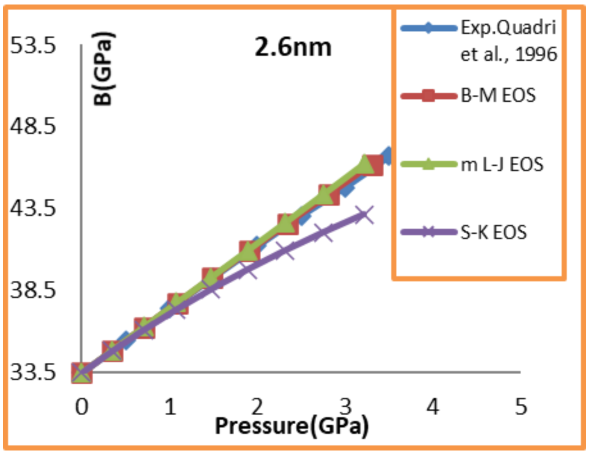
Fig.1(a, b, c): Variations of V/V_0 under high pressure for PbS nano particles (2.6, 5.4, 8.8) nm using (B-M, m L-J, S-K) EOSs in comparison with the experimental data.

Obtained results in Figs.1 (a, b, c) reveal the size dependence of V/V_0 variation under high pressure for PbS nano particles where there is more agreement between obtained results from different EOSs, themselves, and with experimental data as the size of PbS nano particles increases.

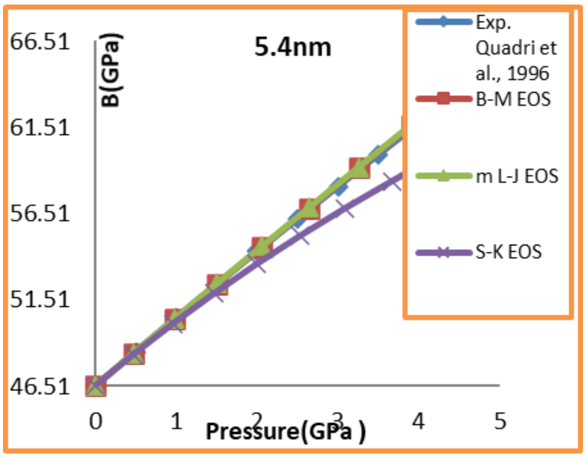
This may be attributed to increase the surface effect for smaller nano particle. On the other hand, S-K EOS result show less agreement as size decreases.

2- Calculation of bulk modulus (B_T) variation under high pressure, for different sizes of PbS nano particles, using different EOSs.

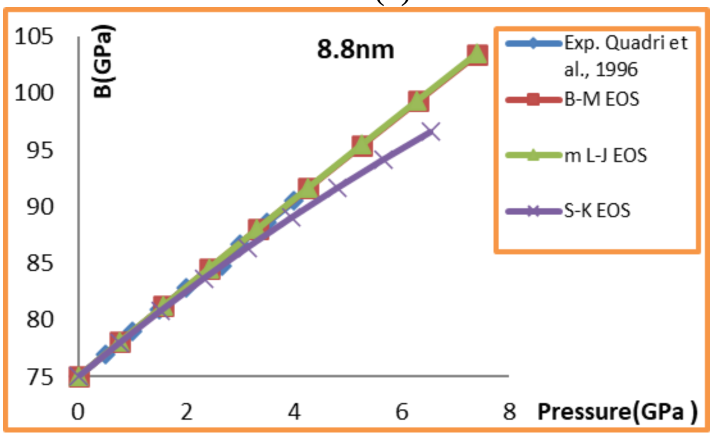
On substituting B_0 , $B_0^{'}$ values from (Table 1) and η values corresponding to different pressure values, from Figs. (1a, b, c) into equations (10,12 and 14) respectively for each PbS nano particle size, Figs. (2a, b, c) show, present obtained results of B_T variation under high pressure for different sizes of PbS nano particles, in comparison with experimental data of (Quadri *et al*, 1996).



(a)



(b)



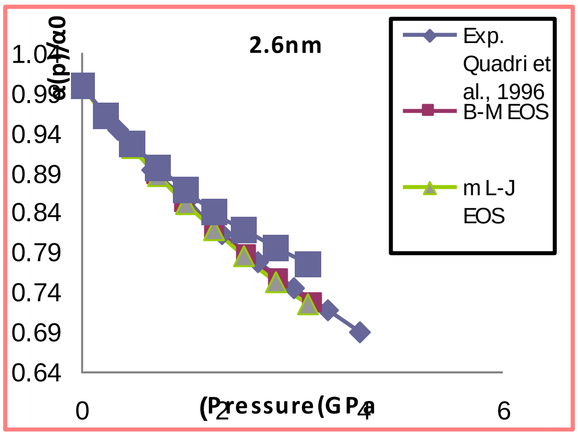
(c)

Figs. 2(a, b, c): Variation of B_T under high pressure for different sizes of PbS nano particles (2.6, 5.4, 8.8)nm using (B-M ,m L-J, S-K) EOSs in comparison with experimental data .

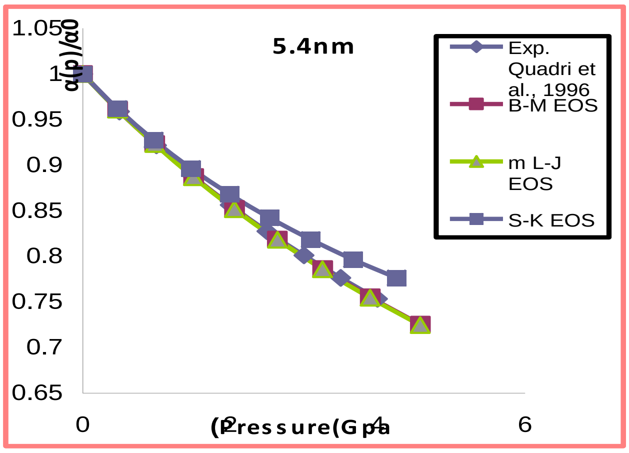
Figs. (2 a, b, c) show that B_T increases under high pressure while B_0 increases with size increasing of nano particle. Obtained results show an exact agreement with themselves and with experimental data. Results obtained by S-K EOS show slight difference from experimental data further to present obtained results by using (B-M, m L-J) EOSs.

3- Calculation of $\alpha(P)/\alpha_0$ variation under high pressure.

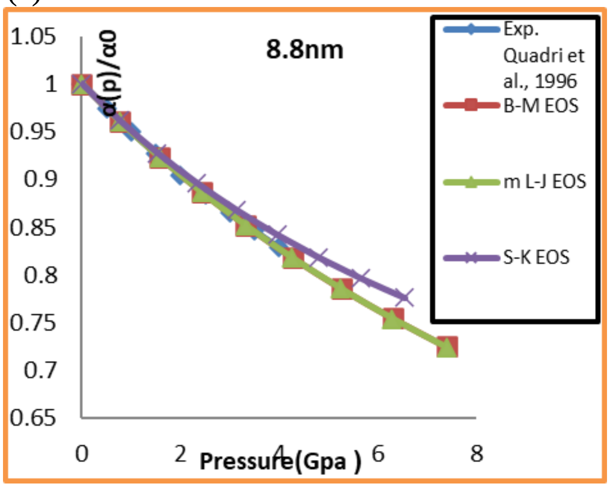
Substituting B_0 and $B_0^{'}$ values, tabulated in (Table 1) for different sizes of PbS nano particles and η values corresponding to different pressure from Figs. (1a, b, c), into equations (16, 19, 21). Figs. (2 a, b, c) show variation of α_r under high pressure for different sizes of PbS nano particles (2.6, 5.4, 8.8) nm. Figs. (3 a, b, c) reveal that α_r decreases under high pressure.



(a)



(b)



(c)

Figs. 3 (a, b, c): Variation of $\alpha(p)/\alpha_0$ under high pressure for different sizes of PbS nano particles (2.6, 5.4, 8.8) nm using (B-M, m L-J, S-K) EOSs in comparison with experimental data

DISCUSSION AND CONCLUSION

PbS nano particles present results for variations of [V/V_0, Figs. (1 a, b, c); B_T, Figs. (2 a, b, c), α_r -Figs. (3 a, b, c)] under high pressure reveal an excellent agreement with experimental data of (Chandra, 2008) specially at the nano particle size 8.8nm. A slight difference between present obtained results and experimental data are shown on using S-K EOS for the nano particle size (5.4, 2.6) nm and these differences increase for smaller size, while all the results obtained by using B-M EOS and m L-J EOS keep their agreements with experimental data. This specifies that the well-known B-M and m L-J EOSs are useful for studying nano materials under high pressure, and puts question mark on the EOS of S-K.

We found that B_0 values are size dependent as it where declare in (Table 1). The bulk modulus, B_T, increases with pressure increasing. While isothermal relative expansion coefficient increases with a decrease in grain sizes of nano PbS particle.

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اعتماد خصائص المرونة الحرارية على حجم كبريتيد الرصاص النانوي(PbS) تحت الضغط العالي

الملخص

يعرض البحث الحالي دراسة نظرية لاستقصاء سلوك الانضغاطية للنانو PbS $(V/V_o, B_T, \alpha_r)$ تحت الضغط العالي باستخدام معادلات حالة مختلفة. ان اعتماد هذه المعلمات على الضغط، لثلاثة احجام مختلفة (2.6nm, 5.4nm, 8.8nm) من جسيمات النانو PbS، قد تم حسابه معادلة الحالة بيرخ–مرنكهان(B-M EOS) و معادلة الحالة لينارد–جونس المحورة (mL-J EOS)، فضلا عن معادلة الحالة ساي–كايو(S-K EOS). تم مقارنة النتائج المستحصلة مع البيانات التجريبية المتاحة. وأظهرت هذه المقارنة امكانية استخدام معادلات الحالة المعروفة للمواد العيانية مثل معادلة الحالة بيرخ–مرنكهان (B-M EOS) و معادلة الحالة لينارد–جونس المحورة (mL-J EOS) فضلا عن معادلة الحالة ساي–كايو(S-K EOS) والتي تستخدم لمواد النانو. في البحث الحالي تم استقصاء تأثير حجم الجسيمات تحت الضغط العالي. النتائج الإجمالية لهذا البحث وضعت علامة استفهام حول معادلة الحالة (S-K).

الكلمات الدالة: نانو PbS، معادلة الحالة، الضغط العالي، جالينا، مواد النانو.