Mechanical and thermal properties of praseodymium monochalcogenides and monopnictides under pressure

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Abstract. The mechanical and thermal properties of praseodymium monochalcogenides and monopnictides are calculated using elastic constants, those have been derived from two body inter-ionic potential theory. We have calculated the Young’s modulus (E), Poisson’s ratio (ν), anisotropy factors (A), sound velocities and Debye temperature (θ_D) for these compounds. The bulk modulus to shear modulus ratio (B/G) lies between 1.75-1.92 for all these compounds, which shows that all compounds are ductile in nature. Young’s modulus shows that PrS and PrAs are stiffer than the other monochalcogenides and monopnictides of praseodymium. The variation of elastic constants (C_{11}, C_{44}) with pressure and the variation of Debye temperature with pressure are also presented for these compounds.

1. Introduction

In recent years, a great deal of interest has been focused on the rare earth chalcogenides and pnictides because they form an interesting and extensively studied series and have numerous applications in technologies [1]. The praseodymium chalcogenides have attracted great attention due to their potential applications in spintronics, spin filtering devices, hyperfine enhanced nuclear cooling, study of combined electron and nuclear ordering phenomenon at very low temperature [2] thus opened a new area for development of electronic devices such as metal base transistors. A few experimental and theoretical studies of praseodymium monochalcogenides and monopnictides are available in literature [1, 3-5]. Shirotani et al. [3] have systematically investigated the pressure induced structural phase transition from NaCl-type (B_1) to CsCl-type (B_2) structure in cerium and praseodymium monopnictides by measuring the powder X-ray diffraction pattern using synchrotron radiation. As far as, the electronic properties of these compounds are concerned, Vaitheeswaran et al. [4] have calculated the electronic structure of praseodymium monochalcogenides and monopnictides under ambient and high pressure. They found that the trivalent Pr configuration is the ground state in all these compounds and remains stable even under pressure up to ~50 GPa. Very recently, Kocak et al. [5] have investigated the structural, elastic and lattice dynamical properties of praseodymium chalcogenides (PrS, PrSe and PrTe) using the VASP code. A systematic structural study of praseodymium monochalcogenides (PrX: X = S, Se, Te) and praseodymium monopnictides (PrY: Y = P, As, Sb, Bi) is reported from our group [1] using the interionic potential theory with necessary modifications. These compounds undergo B_1 to B_2 phase transitions at various pressures [1]. Our further interest in these compounds is motivated for their mechanical and thermal properties. The knowledge of mechanical properties is essential for many practical applications such as load...
deflection, thermoelastic stress, sound velocities, and so on. The mechanical properties such as Young modulus \((E)\), shear modulus \((G)\), Poisson ratio \((\nu)\) and anisotropic ratio \((A)\) and thermal properties such as Debye temperature \(\left(\theta_D\right)\) of praseodymium monochalcogenides and monopnictides have not been sufficiently studied. This lack of information has motivated us to investigate the mechanical and thermal properties of these compounds.

In the present paper, we have investigated mechanical properties such as Shear modulus \((G)\), Young modulus \((E)\), Poisson ratio \((\nu)\), anisotropic ratio \((A)\) and thermal properties with respect to Debye temperature of praseodymium monochalcogenides and monopnictides incorporating data from previous work [1]. We have also presented the variation of elastic constants and of Debye temperatures with pressure for these compounds.

2. Method of calculation

2.1. Calculation of mechanical properties

The mechanical properties such as Shear and Young modulus, Poisson ratio, and anisotropic ratio are calculated using standard formulism as given in equations 1-4. The incorporation of second order elastic constants (SOEC) in the formalism is calculated using classical inter ionic potential theory [6]. The study of SOEC \(C_{11}, C_{12}\) and \(C_{44}\) and their pressure derivatives at 0K is quite important for understanding of the inter-atomic force in solids. The bulk modulus is derived from elastic constants as

\[
B = \frac{1}{3} (C_{11} + 2C_{12}) \quad (1)
\]

In addition another physical quantity, namely the anisotropic ratio \(A\), defined as: \(A=2C_{44}/(C_{11}-C_{12})\) has also been calculated. For an ideal isotropic system, \(A\) is unity and deviation from unity measures the amount of elastic anisotropy. The Poisson’s ratio, \(\nu\) is calculated using the relation:

\[
\nu = \frac{3B - 2G}{2(3B + G)} \quad (2)
\]

where, \(B\) is bulk modulus and \(G\) is average shear modulus. As per Hill [7] average shear modulus, \(G\) is defined as arithmetic mean of Voigt, \(G_V\) and Reuss, \(G_R\) values, which can be expressed in terms of elastic constants as:

\[
G_V = \frac{1}{5} (C_{11} - C_{12} + 3C_{44}) \quad \text{and} \quad G_R = \frac{5(C_{11} - C_{12})C_{44}}{3(C_{11} - C_{12}) + 4C_{44}} \quad (3)
\]

The Young’s modulus, \(E\) is calculated using the expression:

\[
E = \frac{9BG}{3B + G} \quad (4)
\]

2.2. Calculation of Debye temperature \((\theta_D)\)

The Debye temperature \(\left(\theta_D\right)\) is an important physical parameter of solids, which defines a demarcation line between quantum mechanical and classical behaviour of phonons. We have estimated Debye temperature of PrX and PrX compounds using the following expression [8, 9]:

\[
\theta_D = \frac{h}{K_B} \left[ \frac{3n}{4\pi V_a} \right]^{1/3} S_m \quad (5)
\]

where \(h\) is a Plank’s constant, \(K_B\) is Boltzmann’s constant and \(V_a\) is the atomic volume and \(S_m\) is average sound velocity.

3. Results and discussion

Praseodymium monochalcogenides and monopnictides crystallize in simple NaCl-type structure [10]. The ground state properties of these compounds have been studied by Soni et al. [1] from our group.
They have successfully calculated the lattice parameters, bulk modulus and elastic constant of these compounds. Incorporating all the above parameters we have further investigated Young modulus ($E$), shear modulus ($G$), Poisson ratio ($\nu$) and anisotropic ratio ($A$) for these compounds which are given in Table 1.

**Table 1.** Elastic constants ($C_{11}$, $C_{12} = C_{44}$) [1], bulk modulus ($B$), shear modulus ($G$), Young modulus ($E$), Poisson ratio ($\nu$), anisotropic ratio ($A$), calculated values of density ($\rho$ in Kg/m$^3$), the longitudinal, transverse, average sound velocity ($S_L$, $S_T$ and $S_M$ in m/s) and Debye temperature ($\theta_D$ in K) for praseodymium monochalcogenides and monopnictides.

| Solids | $C_{11}$ | $C_{12}$ = $C_{44}$ | $B$ | $G$ | $E$ | $\nu$ | $A$ | $\rho$ | $S_L$ | $S_T$ | $S_M$ | $\theta_D$ |
|--------|-----------|---------------------|-----|-----|-----|-------|-----|-------|-----|-----|-----|-----------|
| PrS    | 233       | 41                  | 105.8 | 58 | 148 | 0.266 | 0.435 | 6.01 | 5626 | 3245 | 3603 | 591       |
| PrSe   | 211       | 31                  | 91.5  | 48 | 123 | 0.275 | 0.349 | 6.87 | 4892 | 2821 | 3132 | 496       |
| PrTe   | 137       | 20                  | 59.5  | 31 | 80  | 0.274 | 0.354 | 7.00 | 3910 | 2255 | 2504 | 373       |
| PrP    | 156       | 34                  | 75.1  | 43 | 109 | 0.257 | 0.564 | 5.49 | 4968 | 2870 | 3186 | 508       |
| PrAs   | 191       | 39                  | 89.9  | 51 | 129 | 0.260 | 0.513 | 6.54 | 4977 | 2876 | 3192 | 500       |
| PrSb   | 117       | 21                  | 53.5  | 29 | 75  | 0.264 | 0.458 | 6.66 | 3804 | 2197 | 2439 | 360       |
| PrBi   | 103       | 20                  | 48.1  | 27 | 68  | 0.261 | 0.496 | 8.53 | 3184 | 1841 | 2043 | 298       |

We can also measure the brittle/ductile behaviour of these compounds by using empirical relation between the calculated bulk modulus and shear modulus. The empirical relation proposed by Pugh [11]. According to Pugh [11] a material is brittle if the $B/G$ ratio is less than 1.75, otherwise it behaves in ductile manner. The present calculated values of $B/G$ are found to be 1.82 for PrS, 1.91 for PrSe, 1.92 for PrTe, 1.75 for PrP, 1.76 for PrAs, 1.84 for PrSb and 1.78 for PrBi. One can clearly notice that these compounds show ductile nature. The Young’s modulus, $E$ defines stiffness of the materials and it is clear from Table 1 that PrS is stiffer than other monochalcogenides of praseodymium; similarly PrAs is stiffer than the other monopnictides of praseodymium. The Poisson’s ratio, $\nu$, defines the stability of solid against shear. The value of Poisson’s ratio lies in between 1 and 0.5; the calculated values of $\nu$ for praseodymium monochalcogenides and monopnictides do not fall in this range and reveals a possibility of instability of structure. The anisotropic ratio, $A$, is a measure of the degree of elastic anisotropy in solid. For an ideal isotropic system, $A$ is unity and deviation from unity measures the amount of elastic anisotropy. The calculated anisotropic ratio for praseodymium monochalcogenides and monopnictides is less than 1 which indicates that these compounds are not elastically isotropic. We have also calculated the pressure dependence of the second order elastic constants, namely $C_{11}$ and $C_{44}$ for praseodymium monochalcogenides and monopnictides in Fig.1.

![Figure 1: Variation of elastic constants with pressure for praseodymium monochalcogenides.](image1)

![Figure 2: Variation of elastic constants with pressure for praseodymium monopnictides.](image2)
Fig. 1 shows the variation of elastic constants with pressure for praseodymium monochalcogenides and in Fig. 2 the variation of elastic constants with pressure for praseodymium monopnictides. As the pressure increases in B\textsubscript{1} phase, C\textsubscript{11} increases linearly but C\textsubscript{44} decreases linearly this shows that C\textsubscript{44} is less sensitive to pressure as compared to C\textsubscript{11} [12]. There is no experimental data available in literature to compare our prediction.

The Debye temperature ($\theta_D$) is an important fundamental parameter closely related to many physical properties such as specific heat, melting temperature and thermal conductivity of solids. The Debye temperatures for praseodymium monochalcogenides and monopnictides are presented in Table 1. It is clear from Table 1 that the Debye temperature decreases with increasing lattice constant and atomic number of the praseodymium monochalcogenides and monopnictides. The calculated values of density ($\rho$ in Kg/m$^3$), the longitudinal, transverse and average sound velocity ($S_L$, $S_T$ and $S_M$ in m/s) for praseodymium monochalcogenides and monopnictides are also listed in Table 1.

We have also calculated the variation of $\theta_D$ with respect to pressure for praseodymium monochalcogenides and monopnictides and predicted them in Fig. 3a and 3b. It is clear from the figure that $\theta_D$ increases as the pressure increases which shows quite normal behaviour for these compounds.

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