



Elastic and mechanical properties of lanthanide monoxides



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ARTICLE INFO

Article history:

Received 18 June 2014

Received in revised form 12 August 2014

Accepted 19 August 2014

Available online 27 August 2014

Keywords:

Rare-earth lanthanides

Elastic constant

Ductility

Debye temperature

ABSTRACT

In this article we communicate theoretical results of the mechanical properties of lanthanide monoxide LnO (Ln = La, Ce, Pr, Nd, Sm, Eu, Tb, Ho, Er and Yb) i.e., bulk modulus, shear modulus, Young's modulus, anisotropic ratio, Kleinman parameters, Poisson's ratio, Lamé's coefficients, sound velocities for shear and longitudinal waves, and Debye temperature. Cauchy pressure and B/G ratio are also investigated to explore the ductile and brittle nature of these compounds. The calculations are performed with the density functional theory based full potential linearized augmented plane waves (FP-LAPW) method. The calculated results reveal that lanthanide based monoxides are mechanically stable and possess good resistive power against elastic deformations. Therefore, these mechanically stable materials can effectively be used for practical applications. The computed DOSs shows the metallic character of these compounds. Contour plots of the electron charge densities are also computed to reveal the nature of bonding in these compounds.

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1. Introduction

Lanthanide based compounds have been extensively studied due to their practical applications in physics, chemistry, medicine and high-tech industry [1–3]. Due to the unfilled 4f orbitals and spin–orbit interactions the adjacent electronic states strongly interact with each other, therefore the characterization of accurate physical properties of the lanthanide compounds is a challenging problem for both, experimentalists and theoretical researchers [4]. Among lanthanide based compounds lanthanide oxides are extensively studied due to their wide range of magnetic, electronic and thermo-chemical as well as thermo-physical properties [5,6]. Lanthanides oxides show interesting properties in optical displays as visible light phosphors [7], used as catalysts [8] and having some applications in solid oxide fuel cells [9].

The lanthanide monoxides (LnO) are the simplest lanthanide based compounds which are found in face-centered cubic (fcc) NaCl structure, like the monochalcogenides, and is experimentally

confirmed in thin films by electron microscopy [10,11]. The striking feature of these compounds is their cell parameters, which decreases regularly along the series (from La to Lu) according to the lanthanide contraction apart from Eu and Yb, for which the larger cell parameters are due to the divalent state of the rare earth which is confirmed by the magnetic properties [12–14]. The particular importance of these compounds is their tuning from metallic trivalent rare-earth monoxides (LaO, CeO, PrO, NdO) to divalent rare-earth monoxides (EuO, YbO) which are semiconductors. Samarium monoxide (SmO) shows unusual character with an intermediate valence [12]. Except EuO, these lanthanide monoxides cannot be synthesized at normal pressure and hence most of these LnO compounds (e.g. LaO, CeO, PrO, NdO and SmO) are synthesized at high pressure (15–80 kbar) and temperature (500–1200 °C) [15]. Due to the complexity in the synthesis of these compounds, very few researchers are working in the challenging field of the study of these compounds.

The lanthanide monoxide molecules have been extensively investigated experimentally using spectroscopic methods including laser based emission and absorption and theoretically with ligand field theory (LFT) as well as various ab initio (MCSCF–MRCI, CISD, etc.) and density functional theory methods (DFT) [16,17]. The mechanical stability of the homogeneous crystals of these

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compounds has long been a subject of discussion in the scientific communities.

The purpose of this work is to add some theoretical understanding to these LnO's (Ln = La, Ce, Pr, Nd, Sm, Eu, Tb, Ho, Er and Yb), in order to fill the gap about the physical properties of these compounds in literature. The calculations are carried out with the all electron full potential linearized augmented plane waves (FP-LAPW) method within the framework of density functional theory (DFT). To the best of our knowledge, these results are the ever first results about the elastic and mechanical properties of these compounds. The data presented here will identify the behavior and effectiveness of these compounds for practical applications. The ductile nature of these compounds is predicted on the basis of the calculated results. We hope that our results will be also helpful in future experimental and theoretical investigations since they reveal many novel physical phenomena.

2. Theory and method of calculations

In the present study, calculations have been performed by using density functional theory (DFT) implemented in the WIEN2k [18] and employing the full potential linearized augmented plane waves (FP-LAPW) method [19]. The exchange correlation effects are calculated within generalized gradient approximation (GGA) scheme of Perdew et al. PBEsol-GGA [20]. For comparison we also use PBE-GGA [21]. To achieve convergence the basis set expand in terms of plane waves up to $R_{MT} K_{max} = 9$, where R_{MT} is the smallest atomic radius in a unit cell and K_{max} is the magnitude of the maximum value of k -vector in the plane wave expansion. For the valence wave function inside a muffin-tin spheres the maximum value of angular momentum is $l_{max} = 10$. In the interstitial region the charge density is Fourier expanded up to $G_{max} = 12$. High accuracy is required to calculate elastic properties, therefore a dense k mesh of 120 k -points are taken in the irreducible wedge of the Brillouin zone with grid size $15 \times 15 \times 15$ using the Monkhorst and Pack mesh [22].

In this work Cubic-elastic software [23] is used to calculate the elastic properties of the lanthanide monoxides. The details about Cubic-elastic software are available in Ref. [24]. The energy approach [25] as implemented in the WIEN2k [18] is used to obtain reliable results. The elastic constants are calculated from the total change in energy of the system by applying small strain ε and can be written in the form of Taylor expansion as:

$$E(V, \varepsilon_i) = E(V_0, 0) - P(V_0)\Delta V + \frac{V_0}{2} \sum_{ij} C_{ij} \varepsilon_i \varepsilon_j + O[\varepsilon_i^3] \quad (1)$$

Here V_0 and $P(V_0)$ are the volume and pressure of the undistorted lattice at volume V_0 . In order to simplify Eq. (1) we must remember that ε_i^3 is higher power and the term $O[\varepsilon_i^3]$ will be neglected. Using Voigt notations by replacing $XX=1$, $YY=2$, $ZZ=3$, $YZ=4$, $ZX=5$ and $XY=6$ and taking into account the additional symmetry imposed by the crystal symmetry; the number of elastic constants are decreased. In particular for a cubic lattice only three independent elastic constants C_{11} , C_{12} and C_{44} are remained. The Taylor expansion of cubic elastic constants in matrix representation can be written as:

$$C = \begin{pmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{pmatrix} \quad (2)$$

The Bulk modulus B_0 is related to elastic constants C_{11} and C_{12} by equation [26]:

$$B_0 = \frac{C_{11} + 2C_{12}}{3} \quad (3)$$

The original cubic system can be deformed by applying the deformation matrix D . The following deformation matrices are used to determine C_{11} , C_{12} and C_{44} [23].

$$D_{ortho} = \begin{pmatrix} 1+\varepsilon & 0 & 0 \\ 0 & 1-\varepsilon & 0 \\ 0 & 0 & \frac{1}{1-\varepsilon^2} \end{pmatrix} \quad (4)$$

$$D_{cubic} = \begin{pmatrix} 1+\varepsilon & 0 & 0 \\ 0 & 1+\varepsilon & 0 \\ 0 & 0 & 1+\varepsilon \end{pmatrix} \quad (5)$$

$$D_{monoc} = \begin{pmatrix} 1 & \varepsilon & 0 \\ \varepsilon & 1 & 0 \\ 0 & 0 & \frac{1}{1-\varepsilon^2} \end{pmatrix} \quad (6)$$

By taking the second order derivative of the energy of distortional orthorhombic deformation (D_{ortho}), volumetric cubic deformation (D_{cubic}) and distortional monoclinic deformations (D_{monoc}), the value of C_{11} , C_{12} and C_{44} can be determined.

The second order derivative of the energy for D_{ortho} is:

$$\frac{d^2 E}{d\varepsilon^2} = 2V_0(C_{11} - C_{12}) \quad (7)$$

The second order derivative of the energy for D_{cubic} is:

$$\frac{d^2 E}{d\varepsilon^2} = 3V_0(C_{11} + 2C_{12}) \quad (8)$$

and the second order derivative of the energy for D_{monoc} is:

$$\frac{d^2 E}{d\varepsilon^2} = 4V_0 C_{44} \quad (9)$$

In addition to elastic constants, Voigt shear modulus (G_V), Reuss shear modulus (G_R), Hill shear modulus (G_H), Young's modulus (Y), shear constant (C'), Cauchy pressure (C''), Poisson ratio (ν), Kleinman parameter (ζ), Lamé's coefficients (λ) and (μ) and anisotropy constant (A) has also been calculated to explain the mechanical stabilities and all elastic properties of the LnO compounds.

3. Results and discussions

3.1. Elastic properties

Elastic properties of a solid are very important, because they can be used in the description of different fundamental solid state phenomena such as intra-atomic bonding, equations of state, and phonon spectra. Elastic properties are also linked thermodynamically with specific heat, thermal expansion, Debye temperature, and Gruneisen parameter. The knowledge of elastic constants is necessary for many practical applications related to the mechanical properties of solids like load deflection, thermoelastic stress, internal strain, sound velocities, and fracture toughness.

The calculated elastic constants of LnO (Ln = La, Ce, Pr, Nd, Sm, Eu, Tb, Ho, Er and Yb) compounds at ambient pressure are given in Table 1. To the best of our knowledge, no theoretical and experimental results are available to compare our results. The stability of the given crystal structure follow certain criteria. The requirement of mechanical stability in a polycrystalline cubic structure leads to the following restrictions on the elastic constants, $C_{11} - C_{12} > 0$; $C_{44} > 0$; $C_{11} + 2C_{12} > 0$. The fulfillment of these criteria's by LnO (Ln = La, Ce, Pr, Nd, Sm, Eu, Tb, Ho, Er and Yb) compounds justify that these are stable against elastic deformations. In order to confirm the stability criteria we calculate the elastic constants of these compounds at different pressures. We concentrate on three parameters $C_{11} - C_{12}$, $C_{11} + 2C_{12}$ and C_{44} , which are related to the structural stability. Fig. 2 shows the variation of $C_{11} - C_{12}$, $C_{11} + 2C_{12}$ and C_{44} against different pressures. The positive values of $C_{11} - C_{12}$, $C_{11} + 2C_{12}$ and C_{44} demonstrate that these compounds are stable against pressure.

3.2. Mechanical properties

The main mechanical parameters, i.e. bulk modulus B_0 , shear modulus G , Young's modulus Y , Poisson's ratio ν and anisotropic ratio A , which are important for industrial applications are calculated by both exchange correlation effects PBEsol-GGA and PBE-GGA from the elastic constants of LnO (Ln = La, Ce, Pr, Nd, Sm, Eu, Tb, Ho, Er and Yb). The calculated results are presented in Tables 1 and 2. As the mechanical parameters calculated by both exchange and correlation effects are very close to each other, therefore we only explain the results obtained by PBE-sol-GGA. These important parameters are used to characterize the mechanical behavior of a material.

The average shear modulus, $G = G_H$, is a measure of resistance to reversible deformations upon shear stress [27]. Therefore, by calculating the shear modulus G , the hardness of a material can be

Table 1
Calculated values of elastic constants C_{11} , C_{12} , C_{44} (in GPa), Bulk modulus B_0 (in GPa), Young's modulus Y (in GPa), Voigt's shear modulus G_V , Reuss' shear modulus G_R and Hill's shear modulus G_H .

Comp.	E_{xc}	C_{11}	C_{12}	C_{44}	B_0	Y	G_V	G_R	G_H	B_0/G
LaO	PBEsol	202.160	47.774	55.760	99.236	158.704	64.333	62.727	63.530	1.562
	PBE	186.971	60.509	66.245	102.663	161.098	65.039	65.006	65.022	1.579
CeO	PBEsol	343.078	85.937	61.442	171.651	226.111	88.293	77.661	82.977	2.069
	PBE	330.450	78.764	57.234	162.659	216.469	84.678	73.197	78.937	2.061
PrO	PBEsol	279.882	80.997	48.224	147.292	178.394	68.711	60.737	64.724	2.276
	PBE	271.882	84.337	50.038	146.852	175.668	67.532	61.514	64.523	2.276
NdO	PBEsol	323.115	87.804	43.114	166.241	190.877	72.931	57.749	65.340	2.544
	PBE	311.102	88.285	50.053	162.557	194.096	74.595	64.194	69.395	2.343
SmO	PBEsol	272.326	20.453	60.714	104.411	203.903	86.803	76.578	81.690	1.278
	PBE	280.311	22.335	55.859	108.327	202.340	85.111	72.242	78.676	1.377
EuO	PBEsol	221.081	23.757	50.630	89.532	166.288	69.843	62.874	66.358	1.349
	PBE	227.347	27.757	46.915	94.287	164.594	68.067	59.533	63.800	1.478
TbO	PBEsol	165.379	114.186	25.319	131.250	71.662	25.430	25.429	25.430	5.161
	PBE	175.810	105.614	22.319	129.013	76.846	27.431	26.124	26.777	4.818
HoO	PBEsol	216.980	71.872	73.404	120.241	182.273	73.064	73.062	73.063	1.646
	PBE	224.709	76.465	69.895	125.880	180.535	71.586	71.527	71.556	1.759
ErO	PBEsol	210.029	76.712	89.943	121.151	197.970	80.629	78.916	79.773	1.519
	PBE	200.626	60.147	87.665	106.973	193.443	80.695	79.751	80.223	1.333
YbO	PBEsol	443.390	142.861	76.185	243.037	277.218	105.817	94.899	100.358	2.422
	PBE	423.332	127.435	70.126	226.067	264.305	101.255	88.813	95.034	2.379

determined more accurately. As per Hill average shear modulus [28], G is defined as the arithmetic mean of Voigt G_V [27] and Reuss, G_R values, which can be expressed in terms of elastic constants as:

$$G_V = \frac{1}{5}(3C_{44} + C_{11} - C_{12}) \quad (10)$$

$$G_R = \frac{5(C_{11} - C_{12})C_{44}}{4C_{44} + 3(C_{11} - C_{12})} \quad (11)$$

$$G_H = \frac{G_V + G_R}{2} \quad (12)$$

The calculated values of G_H are given in Table 1, which indicate that YbO exhibits the largest value of G_H (100.358 GPa) being the most stiffer of all, while TbO is the least stiffer with lower value of shear modulus (25.430 GPa). The other compounds lie in the range between these two values. Young's modulus, Y , is used to find the response of a material to the linear strain along edges and is defined as the ratio between stress and strain. It is used for the measurement of stiffness of a material, i.e. a material will be stiffer if the value of Y is larger. It can be found out from the calculated values of Voigt shear modulus G_V and bulk modulus B_0 by using the following equation:

$$Y = \frac{9B_0G_V}{3B_0 + G_V} \quad (13)$$

The higher values of Young's modulus as compared to Bulk modulus for LaO, CeO, NdO, SmO, EuO, HoO, ErO and YbO indicate that these materials are stiffer than TbO. The variation in bulk modulus, Young's modulus and shear modulus with elastic constants C_{11} , C_{12} and C_{44} are shown in Table 1. It is clear from the table that all the materials have higher values of Young's modulus as compared to the Bulk and shear moduli.

The ratio of bulk modulus to shear modulus (B_0/G) can be used to calculate the ductile/brittle character of a material [29]. If B_0/G ratio is greater than 1.75, then the material will be considered as a ductile otherwise it will be of brittle nature. Pettifor and Chen et al. have demonstrated the brittle versus ductile transition in intermetallic compounds from first principles calculations [30,31]. They demonstrated that the higher the value of B_0/G , the

more ductile the material would be. The B_0/G ratio of LnO (Ln = La, Ce, Pr, Nd, Sm, Eu, Tb, Ho, Er and Yb) are given in Table 1. The table shows that B_0/G ratio of LaO, SmO, EuO, HoO and ErO materials is less than 1.75. Therefore, these compounds are of brittle character. Unlike these brittle compounds, the table also indicates that CeO, PrO, NdO, TbO and YbO are ductile in nature.

The Cauchy pressure is another interesting elastic parameter used to describe the angular characteristic of atomic bonding in a compound [30]. The calculated values of the Cauchy pressure are given in Table 2, where the calculations are carried out by using the following equation:

$$C'' = C_{12} - C_{44} \quad (14)$$

The positive value of Cauchy pressure is responsible for a ionic bonding, while a material with negative Cauchy pressure requires angular or directional character in bonding (covalent bonding). The increase in the negative value of Cauchy pressure leads to the more directional bonding, i.e. lower mobility characteristic of a material. Furthermore, a compound with more negative value of Cauchy pressure will possess more brittle nature. For example, for ductile materials such as Ni and Al, the Cauchy pressures have positive values, while for brittle semiconductors such as Si, the Cauchy pressure is negative. The plot between Cauchy pressure and B_0/G ratio is presented in Fig. 1. It is clear from this figure that materials with positive value of Cauchy pressure exhibit ionic bonding and are less brittle, while material with negative value of Cauchy pressure are of more directional covalent bonding and are more brittle in nature.

Poisson's ratio ν is calculated using the relation:

$$\nu = \frac{3B_0 - Y}{6B_0} = \frac{1}{2} - \frac{Y}{6B_0} \quad (15)$$

Poisson's ratio is the measure of the compressibility, i.e. it is the ratio of lateral to longitudinal strain in uniaxial tensile stress. Typically it ranges from 0.2 to 0.49 and is around 0.3 for most of the materials. Interestingly, as $\nu \rightarrow 1/2$, material tends to be incompressible [32], while at $\nu = 1/2$ the material is nearly incompressible. Its volume remains constant no matter how it is deformed. If $\nu = 0$, then stretching a specimen causes no lateral contraction.

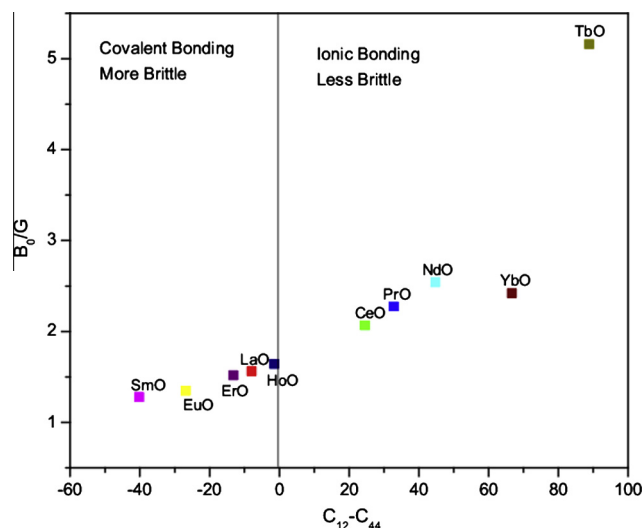
Table 2Calculated values of Shear constant (C'), Cauchy pressure (C''), Lamé's coefficients (λ and μ), Kleinman parameter (ζ), Anisotropy constant (A) and Poisson's ratio (ν).

Comp.	E_{xc}	C'	C''	λ	μ	ζ	A	ν
LaO	PBEsol	77.193	−7.986	56.347	64.333	0.443	0.722	0.233
	PBE	63.231	−5.736	59.303	65.039	0.565	1.048	0.238
CeO	PBEsol	128.571	24.495	116.231	88.293	0.462	0.478	0.280
	PBE	125.843	21.530	106.208	84.678	0.446	0.555	0.278
PrO	PBEsol	99.443	32.773	101.484	68.711	0.516	0.485	0.298
	PBE	93.773	34.299	101.831	67.532	0.546	0.534	0.301
NdO	PBEsol	117.656	44.690	117.621	72.930	0.492	0.366	0.309
	PBE	111.409	38.232	112.827	74.595	0.508	0.449	0.301
SmO	PBEsol	125.937	−40.261	46.542	86.803	0.234	0.482	0.175
	PBE	128.988	−33.524	51.587	85.111	0.239	0.433	0.189
EuO	PBEsol	98.662	−26.873	42.970	69.843	0.274	0.513	0.190
	PBE	99.795	−19.158	48.909	68.067	0.293	0.470	0.209
TbO	PBEsol	25.597	88.867	114.297	25.430	1.161	0.989	0.409
	PBE	35.098	83.295	110.726	27.431	1.001	0.636	0.401
HoO	PBEsol	72.554	−1.532	71.532	73.064	0.576	1.012	0.247
	PBE	74.122	6.570	78.156	71.586	0.589	0.943	0.261
ErO	PBEsol	66.659	−13.231	67.398	80.629	0.626	1.349	0.228
	PBE	70.240	−27.518	53.177	80.695	0.531	1.248	0.199
YbO	PBEsol	150.265	66.676	172.493	105.817	0.563	0.507	0.310
	PBE	147.949	57.309	158.564	101.255	0.533	0.474	0.305

Some bizarre materials have $\nu < 0$, if you stretch a round bar of such a material, the bar increases in diameter. The calculated values of Poisson's ratio for LnO (Ln = La, Ce, Pr, Nd, Sm, Eu, Tb, Ho, Er and Yb) are presented in Table 2. It is clear from the table that these values vary between 0.409 and 0.175, which indicates that these materials are less compressible and are stable against external deformation. Furthermore, Poisson's ratio also provides more information about the characteristics of the bonding forces [33]. For central forces in solids, the lower limit of ν is 0.25 and upper limit of ν is 0.5 [33]. The table shows that the values of Poisson's ratio for CeO, PrO, NdO, TbO and Yb fall in this limit, which demonstrates that the interatomic forces in these compounds are central forces.

The anisotropic ratio for a material is obtained by using the following equation:

$$A = \frac{2C_{44}}{C_{11} - C_{12}} \quad (16)$$

**Fig. 1.** Relation between Pugh ratio (B_0/G) and Cauchy pressure $C_{12} - C_{44}$ (GPa).

The anisotropic ratio (A) is a measure of the degree of elastic anisotropy in a solid. For an ideal isotropic system, A is unity and deviation from unity measures the amount of elastic anisotropy. From Table 2, we can see that the calculated anisotropic ratio for LnO (Ln = La, Ce, Pr, Nd, Sm, Eu, Er and Yb) deviate from 1, which specify that these compounds are not elastically isotropic and their properties vary in different directions. Unlike other compounds the anisotropic ratio for HoO and TbO slightly deviates from unity, which shows the isotropic behavior of these materials.

The internal strain of a material can be quantified by a parameter ζ introduced by Kleinman [34]. It describes the relative ease of bond bending versus the bond stretching. Minimizing bond bending leads to $\zeta = 0$, while, minimizing bond stretching leads to $\zeta = 1$. The Kleinman parameter is linked to the elastic constants by the following equation:

$$\zeta = \frac{C_{11} + 8C_{12}}{7C_{11} - 2C_{12}} \quad (17)$$

Our calculated values of Kleinman parameter predict that in LaO, CeO, NdO, SmO, EuO and TbO compounds, bond bending is dominated (ζ falls between 0 and 5), while in PrO, HoO, ErO and YbO compounds the bond stretching is dominated (ζ is close to 1).

The other interesting elastic parameters are Lamé's constants (λ, μ) which depend on a material and its temperature. Lamé's constants can be calculated from Young's modulus and Poisson's ratio by using the following equations:

$$\lambda = \frac{Y\nu}{(1+\nu)(1-2\nu)} \quad \text{and} \quad \mu = \frac{Y}{2(1+\nu)} \quad (18)$$

For higher value of Young's modulus the larger values are for Lamé's coefficients. The two parameters together constitute a parameterization of the elastic moduli for homogeneous isotropic media. λ is known as Lamé's first constant and μ is Lamé's second constant. The values of the Lamé's coefficients for LnO (Ln = La, Ce, Pr, Nd, Sm, Eu, Tb, Ho, Er and Yb) are given in Table 2. Our results show that Lamé's second modulus is equal to Voigt's shear modulus (i.e. $\mu = G_V$). For isotropic materials $\lambda = C_{12}$ and $\mu = C'$. The results presented in Table 2 reveal that out of all the oxides HoO and TbO satisfies these conditions and hence are isotropic materials.

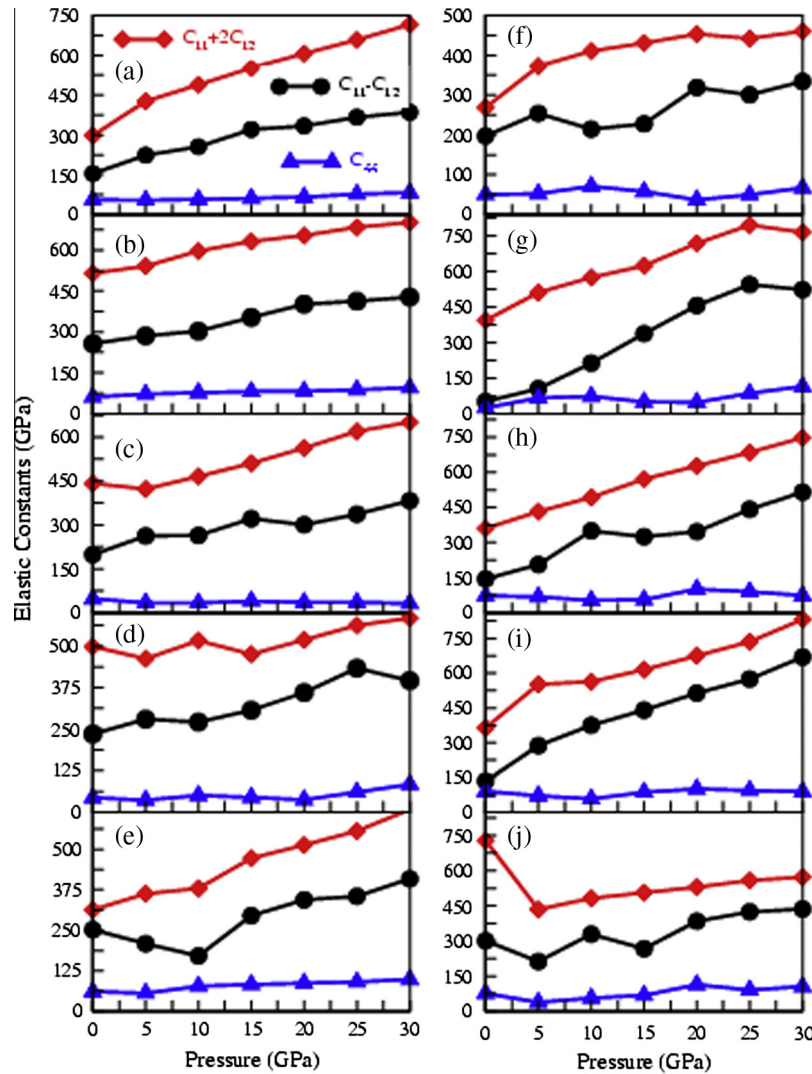


Fig. 2. Variation of $C_{11} - C_{12}$, $C_{11} + 2C_{12}$ and C_{44} against different pressures for (a) LaO, (b) CeO, (c) PrO, (d) NdO, (e) SmO, (f) EuO, (g) TbO, (h) HoO, (i) ErO, and (j) YbO.

Shear constant (C'), also known as tetragonal shear modulus, is another important parameter of a compound, which defines the dynamical stability of the compound and can be calculated by using the following relation:

$$C' = \frac{1}{2}(C_{11} - C_{12}) \quad (19)$$

The calculated values for the shear constants of the lanthanide monoxides under investigation are given in Table 2. The dynamical stability of a compound requires that $C' > 0$, while the negative value of C' is the indication of instabilities with respect to the tetragonal distortion, which is in accordance with the experimental outcome [35,36]. The positive values of the lanthanide monoxides in the table indicate that these materials are mechanically stable.

3.3. Sound velocities and Debye temperature

The Debye temperature is an important fundamental parameter closely related to many physical properties such as elastic constants, specific heat and melting temperature. Once Young's modulus, Bulk modulus, and shear modulus are known then it can be easily calculated, using the following classical relations [37]:

$$\theta(D) = \frac{h}{k_B} \left[\frac{3n}{4\pi} \left(\frac{N_A \rho}{M} \right) \right]^{\frac{1}{3}} v_m \quad (20)$$

where h is plank constant, k_B is Boltzmann constant, N_A is Avogadro's number, ρ is the density, M is the molecular weight, v_m is the average sound velocity and n is the number of atom per formula unit. The average sound velocity in the polycrystalline material is approximately given by [38]:

$$v_m = \left[\frac{1}{3} \left(\frac{2}{v_s^3} + \frac{1}{v_l^3} \right) \right]^{-\frac{1}{3}} \quad (21)$$

where v_l and v_s are the longitudinal and transverse sound velocities which can be obtained using the shear modulus G and the Bulk modulus B_0 from Navier's equation [39]:

$$v_l = \left[\frac{B_0 + \frac{4G}{3}}{\rho} \right]^{\frac{1}{2}} \quad \text{and} \quad v_s = \left[\frac{G}{\rho} \right]^{\frac{1}{2}} \quad (22)$$

The calculated values of sound velocity, for longitudinal and shear waves (v_l and v_s), and Debye average velocity (v_m) for LnO (Ln = La, Ce, Pr, Nd, Sm, Eu, Tb, Ho, Er and Yb) compounds are presented in Table 3. No data is available in literature for comparison.

The sound velocities depend on the elastic moduli via Bulk modulus (B_0) and shear modulus (G) of a material. Thus, for a material having larger elastic moduli means higher sound velocity.

3.4. Density of states (DOSs) and charge densities

Total and partial densities of states (DOSs) have been calculated with PBEsol-GGA as exchange correlations potential to have further insight into the bonding nature of LnO (Ln = La, Ce, Pr, Nd, Sm, Eu, Tb, Ho, Er and Yb). The results are presented in Fig. 3(a–j). In all LnO compounds the metallic behavior is observed with no gap between valence band and conduction band and the Fermi level is crossed with a high intensity mainly by the Ln elements. The dominating characters of f states are observed in all these compounds. The results show that in occupied states the core states are mainly due to the p state of oxygen. The p state of oxygen is lower in energy than the f and d states of lanthanides; hence the p state of oxygen is more localized. The f state are closer to the Fermi level, shows more itinerant character. The bands at the top

Table 3

The calculated values of density (ρ in g/cm³), sound velocity of transverse, longitudinal and average sound velocity (v_s , v_l and v_m m/s), and Debye temperature ($\theta(D)$ in K) of these compounds.

Comp.	ρ	v_l	v_s	v_m	$\theta(D)$
LaO	7.71	4884.42	2870.52	3181.74	467.17
CeO	8.33	5821.34	2761.63	3106.95	466.90
PrO	8.70	5181.65	2702.27	3023.48	460.20
NdO	8.77	5374.89	2691.46	3019.05	457.57
SmO	9.06	4852.40	2648.04	2953.33	446.89
EuO	8.95	4459.74	2664.26	2948.56	442.94
TbO	10.50	3966.00	2459.76	2711.92	423.86
HoO	11.10	4428.19	2392.36	2670.16	420.38
ErO	11.57	4434.43	2343.27	2619.48	416.38
YbO	11.72	5670.47	2328.22	2635.09	416.32

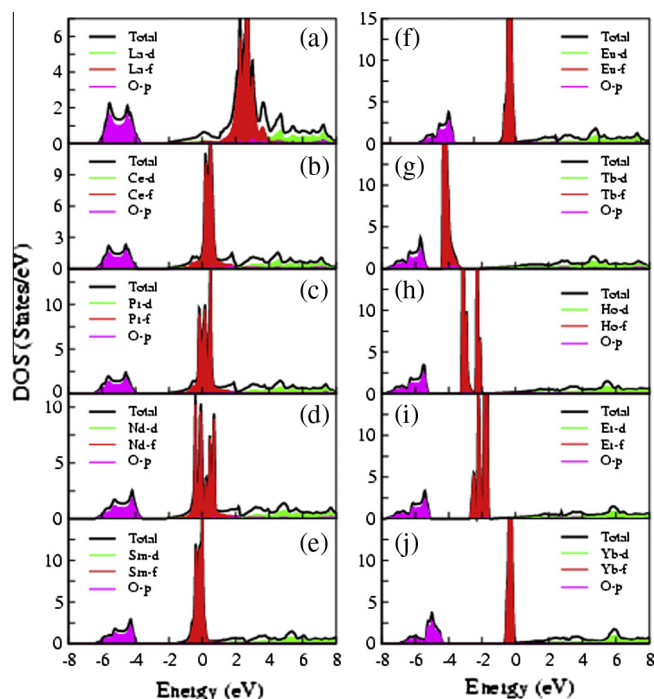


Fig. 3. The total and partial DOS of (a) LaO, (b) CeO, (c) PrO, (d) NdO, (e) SmO, (f) EuO, (g) TbO, (h) HoO, (i) ErO, and (j) YbO.

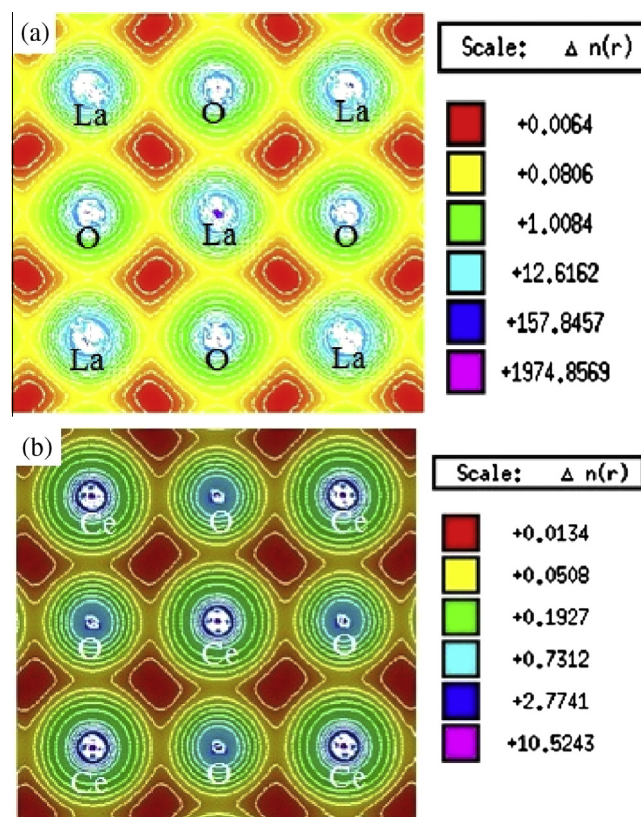


Fig. 4. (a) The contour plot of the electron charge density in (100) plane for (a) LaO and (b) CeO. $\Delta n(r)$ is the variation of the electron charge density as a function of distance away from an atomic site.

of the valence states are due to the f states electrons of rare-earth elements and play key role in bonding.

The charge density distribution is an important property of solid materials and provides good information about the chemical bonding. Fig. 4 shows the contour plots of the distribution of the electron charge densities of LnO along the (100) plane. The intensity of charge density is shown in thermo-scale in which the red color corresponds to the low charge density, while the magenta color shows maximum intensity. It is clearly seen from Fig. 4 that the electronic cloud is mostly distributed around the lanthanides nuclei. Fig. 4(a) shows the electron density of LaO. The covalent La–O bonds are clearly visible in the charge density map in the (100) plane. The covalent bond also exists in SmO, EuO, ErO and HoO compounds. Fig. 4(b) shows the counter plot of CeO. The appearance of spherical symmetry in charge density suggests ionic character in the chemical bonding between Ce–O atoms, which depends on the large electronegativity difference of Ce(0.79) and O(3.44) atoms. The same ionic bond behavior is also observed in PrO, NdO, TbO and YbO.

4. Conclusions

First principle calculations have been performed to study the elastic and mechanical properties of lanthanide monoxides, LnO (Ln = La, Ce, Pr, Nd, Sm, Eu, Tb, Ho, Er and Yb) using FP-LAPW method. The results show that these compounds are elastically stable and anisotropic. The higher values of Young's modulus than Bulk modulus and shear modulus indicate that LaO, CeO, NdO, SmO, EuO, HoO, ErO and YbO are stiffer than TbO. The values of anisotropy constant for these materials deviate from unity. The values of Poisson's ratios vary between 0.23 and 0.409, which

indicate that these materials are less compressible and are stable against external deformation. Poisson's ratios also show that the intra-atomic forces in these compounds are central forces. The sound velocities and Debye temperatures are also calculated for these compounds. The contour plots of the electron charge densities confirm the covalent nature of bonding in LaO, SmO, EuO, ErO and HoO and ionic bonding in CeO, PrO, NdO, TbO and YbO.

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