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Elastic and mechanical properties of lanthanide monoxides

M. Shafiq [a,b], Suneela Arif [c], Iftikhar Ahmad [a,b,*], S. Jalali Asadabadi [d], M. Maqbool [e], H.A. Rahnamaye Aliabad [f]

[a] Center for Computational Materials Science, University of Malakand, Chakdara, Pakistan
[b] Department of Physics, University of Malakand, Chakdara, Pakistan
[c] Department of Physics, Hazara University, Mansehra, Pakistan
[d] Department of Physics, Faculty of Science, University of Isfahan, Hezar Gerib Avenue, Isfahan 81744, Iran
[e] Department of Physics & Astronomy, Ball State University, Muncie, IN 47306, USA
[f] Department of Physics, Hakim Sabzevari University, Sabzevar, Iran

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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, Lame'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.

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

* Corresponding author at: Center for Materials Modeling and Simulations, University of Malakand, Chakdara, Pakistan. Tel.: +92 332 906 7866.
E-mail addresses: ahma5532@gmail.com, dr.iftikhar@uom.edu.pk (I. Ahmad).

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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 Perdrew 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:

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

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:

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

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

$$B_0 = \frac{C_{11} + 2C_{12}}{3} \tag{3}$$

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].

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

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

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

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_{mono}), the value of C_{11}, C_{12} and C_{44} can be determined.

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

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

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

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

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

$$\frac{d^2E}{d\varepsilon^2} = 4V_0C_{44} \tag{9}$$

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), Lame'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