IOP Publishing Mater. Res. Express 5 (2018) 105702 https://doi.org/10.1088/2053-1591/aad9eb

Materials Research Express

RECEIVED
7 June 2018

REVISED
7 August 2018

ACCEPTED FOR PUBLICATION
13 August 2018

PUBLISHED
24 August 2018

PAPER

DFT understandings of structural properties, mechanical stability and thermodynamic properties of $BaCfO_3$ perovskite

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Keywords: half-metallicity, perovskites, electronic structure, thermal properties, mechanical properties

Abstract

Electronic structure, mechanical stability, magnetic and thermal properties of $BaCfO_3$ perovskite have been investigated by density functional theory calculations using full potential linearized augmented plane wave method. The structural optimizations reveal the agreement of lattice parameter with the experimental data. The electronic structure and magnetic properties were precisely determined by generalized gradient approximation (GGA), and Hubbard approximation ($GGA + U$) methods. The electronic structure portrays the half-metallic nature for the compound in both the applied approximations. The total magnetic moment calculated via the above methods was found to be large and integral in nature (6 μB), which also is an indication of the half-metallic character of this material. The mechanical stability has been determined by the calculated elastic constants in addition to the preclusion of mechanical properties like the Young modulus (Y), Bulk modulus (B), the Shear modulus (G) and the Poisson ratio (ν). The observed data of B/G and Cauchy pressure (C_{12}–C_{44}) for the present material reveal its ductile nature. The thermodynamic parameters including heat capacity, thermal expansion, and Debye temperature and their variation w.r.t temperature and pressure (0 K to 500 K and 0 GPa to 40 GPa) has been examined. The melting temperature of 1791.94 ± 300 K for this material was also calculated.

Introduction

The perovskites generally expressed as ABO_3 find immense interests due to their appealing material characteristics and the tuneable physical properties. Such type of materials exhibit temperature and pressure induced structural distortions, different charge-spin orderings and therefore, find various technological applications such as water splitting [1], photocatalysts [2], electrode materials [3], optoelectronic devices [4], thermoelectrics [5] and many more to count here. Moreover, the structural phase transitions in the perovskites, which are fundamental in comprehending the exhibited material properties, led by quantum fluctuations may induce interesting ferroelectrics phenomenon [6]. Keeping this in mind, perovskites prove to be essential material candidates for novel applications and therefore attract large attention from industry as well as technology.

Actinide based perovskite oxides have been synthesised a very long ago, but the understanding of their basic properties is restricted by their active nature and chemical instability. The *f*-electronic states in such systems, interplay with the chemical bonds; and play a crucial role in defining the magnetic phenomenon and crystal structure distortions. Thus, to predict their electronic structure via magnetic and lattice structure investigations turns out to be a stimulating task. On the other hand, DFT calculations provide an alternative to reproduce the approximate understandings of their electronic structure, magnetism and mechanical properties as this technique has been well accepted due to its promising results [7–10]. In the recent past, considerable attention has been paid to such perovskites of ABO_3 kind; $BaAmO_3$ [11] $BaNpO_3$ [12], $BaUO_3$ [13], $BaPaO_3$ [14], $BaPuO_3$ [15], etc. All these oxides are said to be ferromagnetic half-metals with a dominant populated Ac-*f* states at the fermi level. In the cubic phase of $BaCfO_3$, Cf cations will occupy center of the oxygen octahedron and Ba occupy a site that is 4-fold coordinated with O atoms. In early 90's, the experimental growth of $BaCfO_3$ have been found to exhibit the cubic structure within Pm-3m symmetry group [16]. But, no further information is available on this compound and hence we attempted to fill this gap by studying this oxide via first-principles method. For that reason, the present work has been undertaken to investigate the undecided electronic structure and other ground state properties of this material.

Computational details

The cubic $BaCfO_3$ (space group: Pm-3m) perovskite structures are fully relaxed and optimized. The optimized structures are then utilized in computing the structural, electronic and magnetic properties using different schemes, viz generalised gradient approximation (GGA) [17] and onsite Hubbard approximation (GGA + U) [18] as programmed in Wien2K [19]. The GGA + U potential is famous to improve band gap, as the local density (LDA) and generalized gradient (GGA) approximations underestimate the energy gap. The U was varied from 0–7 eV and the optimized value of U for $BaCfO_3$ is 6.2 eV. Moreover, the product of muffin-tin radius (R_{MT}) and maximum wave vector (K_{max}) is set as 7. We take the angular momentum vector $l_{max} = 10$ and Gaussian factor $G_{max} = 12$. To achieve the convergence, the k-mesh of $10 \times 10 \times 10$ is used. Repeated iterations are employed to get convergence, until difference in energy between the consecutive iterations is $<10^{-4}$ Ry. The structure converged with GGA is used to calculate the elastic parameters as in [20].

Results and discussion

Structural properties

The PBE-GGA functional is employed to calculate the structural parameters of $BaCfO_3$ compound. The ground state cubic (Pm-3m) phase with atomic coordinates as Ba (0, 0, 0), Cf (1/2, 1/2, 1/2) and O (0, 1/2, 1/2) is relaxed. For the varying unit cell volumes, the released energies have been observed by optimization process to elucidate the ground state structural parameters. The optimization plot is in antiferromagnetic (AFM), ferromagnetic (FM) and nonmagnetic (NM) configurations is shown in figure 1. The relative stability in FM phase is therefore confirmed from the total energies. The lattice parameters and bulk modulus are extracted by fitting the computed data points with Murnaghan equation and the calculated values are presented in table 1. The observed lattice constant is very close to the experimental results [16]. The calculated bond-lengths are employed to define the reliable structure of a perovskite and thus, the tolerance factor (*t*) is obtained using the Goldschmidt relation $t = 0.707(\mathrm{Ba{-}O})/(\mathrm{Cf{-}O})$ [3, 9]. Here, (Ba–O) is the length between Ba and O atom and (Cf–O) is the length between Cf and O atom in the crystal structure. Generally, for materials with an ideal cubic structure, $t = 0.9$–1.0; for an orthorhombic or rhombohedral structure, $t = 0.71$–0.9. If ($t > 1$), materials will have hexagonal or tetragonal structures and different structures are formed, if ($t < 0.71$) [12]. The observed *t* value comes out to be 0.99 and hence preserves the cubic symmetry of this material.

Another parameter, called Critical radius (r_C) defined as the narrowest passage through which the oxygen ion can migrate along the crystal is also computed for this material and is directly linked to the composition of the perovskite. It plays an important role in the activation energy of oxygen migration and therefore the ionic conductivity. It also offers a guideline for the selection of a dopant ion to tailor the desirable properties. For characteristic perovskite compounds this critical radius does not exceed 1.05 Å. Since, the ionic radii of oxygen ion in the six-fold coordination is 1.4 Å, therefore a substantial outward relaxation of the cations must be present, which could possibly reduce the repulsive overlap interactions [21]. Hence, the oxygen ion during the diffusive jump may temporarily adopt threefold coordination at the position between two A and one B-site cations. But, the threefold coordination of the oxygen ion would offer much large radius (1.36 Å) and the thermal vibration of the cations is supposed to contribute towards the oxygen ion migration energy to pass through the gap. The reduction in mass of the cations directly increases the amplitude of their thermal vibration and, therefore, enhances the oxygen ionic conductivity [22]. The critical radii for the present material is calculated by using the following mathematical formula [21–23]:

$$r_C = \frac{a_0\left(\frac{3}{4}a_0 - \sqrt{2}\,r_B\right)r_B + r_B^2 - {r_A}^2}{(2r_A - r_B) + \sqrt{2}\,a_0}$$

where, a_0 is the lattice constant, r_A and r_B is the ionic radii of Ba and Cf atoms, respectively. Greater the value of critical radius, smaller is the migration activation energy so that minimum lattice disturbance occurs. The