Materials Chemistry and Physics 205 (2018) 315–324

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

First – principles calculations on stability and mechanical properties of various ABO_3 and their alloys

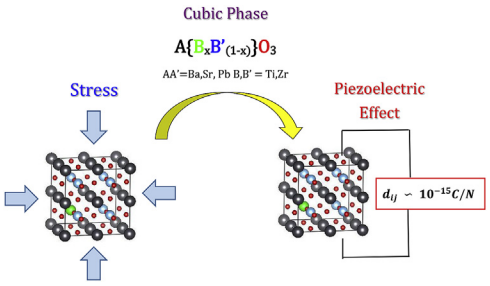
B. Akgenc [a, b, *], A. Kinaci [c], C. Tasseven [d], T. Cagin [b]

[a] Department of Physics, Kirklareli University, Kirklareli, 39960, Turkey
[b] Department of Material Science and Engineering, Texas A&M University, College Station, TX 77845, USA
[c] Argonne Natl Lab, Nanoscale Mat, Lemont, IL 60439, USA
[d] Department of Physics, Yildiz Technical University, Istanbul, 34210, Turkey

HIGHLIGHTS

- Structure, elastic and dielectric properties of ABO_3 type ceramics were calculated.
- Composition and atomic configuration are effected on pizeoelectric properties.
- Our computations highlighted that developed small polarization even if cubic form.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 31 May 2017
Received in revised form
5 November 2017
Accepted 12 November 2017
Available online 16 November 2017

Keywords:
Piezoelectric ceramics
ABO3 type perovskites
Mechanical properties
Structural properties
Piezoelectric properties
Density functional theory

ABSTRACT

In this study, we perform first–principle calculations based on density functional theory (DFT) to obtain the ground state structural, elastic and dielectric properties of various ABO_3 type ceramics and their $\{A_xA'_{(1-x)}\}BO_3$ and $A\{B_xB'_{(1-x)}\}O_3$ alloys. To represent alloy perovskites, we employ supercells with species A, A' = Ba, Sr, Pb; B, B' = Ti, Zr. The effects of composition and atomic configuration/order on lattice structure, thermodynamics, elastic constants and dielectric properties are evaluated. In calculations, we have used linear response and homogeneous field methods and we have also provided an assessment of the performance of these approaches in the determination of aforementioned properties.

We have computed dielectric and piezoelectric properties for the cubic form of alloy perovskites. Even though cubic form of alloy perovskites does not have any piezoelectric properties, owing to crystallographic site occupied by different type of atoms, the inversion symmetry breaks down and the structures develop a small tetragonality, in turn a small polarization and non-zero but quite small piezoelectric coefficients emerge as expected. For instance the observed maximum piezoelectric constant for $BaZr_{(1-x)}Ti_xO_3$ is $0.554x10^{-15}C/N$. The magnitudes are smaller than the feasible ranges for actual application needs, but they may increase substantially upon phase to lower symmetry tetragonal forms transformation.

1. Introduction

ABO_3 type pure perovskite crystals have been extensively studied; however, the structural, elastic, dielectric and piezoelectric

* Corresponding author. Department of Physics, Kirklareli University, Kirklareli, 39960, Turkey.
E-mail address: berna.akgenc@klu.edu.tr (B. Akgenc).

https://doi.org/10.1016/j.matchemphys.2017.11.026
0254-0584/

properties of their alloys are still a subject of inquiry [1–6]. The solid solutions of perovskites, owing to their tunable dielectric and piezoelectric responses, are of great technological interest for industrial and commercial applications such as high-dielectric constant capacitors, ferroelectric thin film memory devices, sensors, switches, actuators, piezoelectric sonars, atomic microscopes, ultrasound generators, piezoelectric motors, ink-jet printers and fuel injectors [7–12]. There are two ideal ways of tuning physical properties of these ABO_3 type perovskite alloys by adjusting the concentration and configuration/order of doped atoms [13–15].

The elastic constants are used to characterize the mechanical response of materials to external macroscopic stress. These constants are closely related to interatomic bonding, mechanical stability, thermal relaxation and internal strain. Studying elastic constants is essential to understand the electromechanical response of perovskite oxide ferroelectrics [16]. Especially today's highly efficient density functional theory (DFT) calculations, being a fast alternative to experiments, can be utilized to scan through many materials for required properties. Elastic constants and related mechanical properties i.e. bulk modulus, shear modulus, Young's modulus, and Poisson's ratio of a large number of complex ceramic crystals with different crystal symmetries have been calculated by means of density functional theory [17]. The main challenge in estimating elastic constants from first principles requires an accurate method to calculate the total energy [18–20]. The results presented here are obtained within the generalized gradient approximation (GGA).

Density functional perturbation theory (DFPT) is another method, which provides the desired response properties in automated, systematic and reliable fashion [21]. Therefore, it has been widely used in calculations of structural, mechanical and electronic properties of perovskite materials and their alloys. DFT study of $ATiO_3$ compounds, where A represents the atoms Ca, Sr, Ba, Ra, Cd, Mg, Ge, Sn and Pb, have revealed that the geometrical size and the configuration of outer electronic shell of A atoms are responsible for determining the off-center positioning of the A atoms [1]. Gonzalez-Garcia et al. have investigated the effect of substituent concentration on structural parameter, band gap energy, mixing enthalpy and phase diagram of $In_{1-x}B_xP$ semiconductor alloys. It has been found that the lattice parameters of the $In_{1-x}B_xP$ alloys decrease with x, B-concentration, showing a negative deviation from Vegard's law, while the bulk modulus increases with composition x, showing a large deviation from the linear concentration dependence [22]. Theoretical analysis has been carried out in $In_xAl_{1-x}N$ alloys on the applicability of Vegard's linear rule and deviations from its linearity with respect to composition, in piezoelectric polarization, surface orientation and degree of strain. To determine and estimate these properties correctly is of vital importance in technological applications of these materials [23]. It has been found that $Bi(Zn_{1/2}Ti_{1/2})O_3$ and PZT solid solution display extremely large cation displacements and leading to tetragonality. The displacements on A site are more pronounced than B-site displacements [24]. J. Bennett et al. have investigated ground state structural properties of $Sn(Al_{1/2}Nb_{1/2})O_3$ (SAN) solid solution and demonstrated that these alloys can be synthesized due to their favorable thermodynamics, and they possess enhanced ferroelectric, and piezoelectric properties [25]. Halilov et al. have investigated the main instabilities in $CdTiO_3$ and $Cd_{0.5}Pb_{0.5}TiO_3$ to show the piezoelectric potential of this perovskite alloy which may provide much larger energy density than traditional composition [26]. Majority work in the field, which has mainly focused on B-site alloying, we have investigated on A-site alloying in addition to B-site. We have constructed $\{A_xA'_{1-x}\}BO_3$ and $A\{B_xB'_{1-x}\}O_3$ alloys for which x is varied from 0 to 1 with the species A, A' = Ba, Sr, Pb; B, B' = Ti, Zr. We have shown the effects substitutions at A-atom site and B-atom site by quantifying properties of these alloys namely their structural properties, elastic constants, dielectric constants, and Born effective charges.

In recent years, researchers have focused on lead-free ABO_3 type perovskite ceramics for technological applications [27–29]. Substantial effort spent on elucidating the influence of alloying on emerging structures and associated enhanced physical properties. As an example, Yang et al. reported the effects of B-site cations on the structure, elastic and thermodynamic properties of $KNa_{0.5}Nb_{0.5}O_3$ perovskite ceramic based on first principle calculations [30]. Pontes et al. have investigated effect of A-site chemical doping on the different properties of $Pb(Ca,Ba)TiO_3$, $Pb(Sr,Ba)TiO_3$ and $Pb(Sr,Ca)TiO_3$ perovskite ceramics through combined experimental and theoretical studies [31]. Riborino et al. conducted a computational mapping of structural, electronic and dielectric properties of lead-free SZT [27]. In the light of these very recent studies, there is still need for a comprehensive DFT study on $AA'BB'O_3$ perovskite structure. Hence, in this work, we study the effects of A-site and B-site cations of $AA'BB'O_3$ type perovskites for wide concentration/configurations. The specific aim of this study is to investigate the effects of alloying (concentration and structural/chemical anisotropy) on their thermodynamic, structural, mechanical, and electromechanical properties for broad concentration ranges rather than providing comprehensive data for pure ABO_3 compounds for various existing polymorphs.

2. Computational method

The first-principles calculations are performed by employing generalized gradient approximation (GGA) based on density functional theory (DFT) which allows ground-state and mechanical property calculations and density functional perturbation theory (DFPT) that lets to calculate of Born-effective charges, dielectric and piezoelectric tensors as implemented in Vienna *abinitio* Simulation Package (VASP) program [32]. The 5*s*5*p* and 6*s* of Ba, $3s, 3p, 3d$and 4*s* of Ti, 2*s*and 2*p* of O, $5d, 6s$and 6*p*of Pb, $4s, 4p$and 5*s* of Sr and $4s, 4p, 5s$ and 4*d* of Zr are considered as valence states in the construction of the pseudopotentials. In any accurate first principle simulation, it is necessary to test the accuracy of exchange-correlation potential forms, and sufficiently large *k*-point meshes and energy cut-off value [33]. Energy convergence tests have been carried out to determine the cut-off energy and the number of *k*-points for all structures. The total energy is converged at the cut-off energy of 520 eV for all structures. The Brillouin-zone integration is done using special *k*-points sampled within the Monkhorst-Pack scheme. It is found that a mesh of 8*x*8*x*8 *k*-points is required to describe well stability and mechanical properties in the cubic structures. In order to optimize computational cost, a $(2 \times 2 \times 2)$ supercell, which contains 40 atoms (eight formula units) is employed. As the system size doubled in each direction the k-point mesh is reduced to 4*x*4*x*4in reciprocal space. In order to make comparisons standard all results for extensive variables such as volume, energy, etc. are reported for one formula unit. All calculations are performed on charge neutral systems and with the following common parameters: (1) a high accuracy for electronic ground-state convergence ($10^{-4}eV$); (2) a small tolerance for ionic relaxation convergence ($-10^{-3}eV$); and (3) maximum ionic steps of 100 for all cases. While using energy minimization, the unit cell parameters and atomic coordinates are allowed to relax.

2.1. Construction of alloys

The prototype of ABO_3 type perovskite structure has a space group of $Pm3'm$ space group (No: 225). Ba, Sr, Pb are considered for atoms of A-sites; Ti and Zr are considered for atoms of B-sites. We