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Ab initio study of electronic structure, elastic and optical properties of anti-perovskite type alkali metal oxyhalides

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ABSTRACT

We report the structural, elastic, electronic, and optical properties of antiperovskite alkali metal oxyhalides Na_3OCl, Na_3OBr, and K_3OBr using two different density functional methods within generalized gradient approximation (GGA). Plane wave pseudo potential (PW-PP) method has been used to calculate the ground state structural and elastic properties while the electronic structure and optical properties are calculated explicitly using full potential-linearized augmented plane wave (FP-LAPW) method. The calculated ground state properties of the investigated compounds agree quite well with the available experimental data. The predicted elastic constants using both PW-PP and FP-LAPW methods are in good accord with each other and show that the materials are mechanically stable. The low values of the elastic moduli indicate that these materials are soft in nature. The bulk properties such as shear moduli, Young's moduli, and Poisson's ratio are derived from the calculated elastic constants. Tran–Blaha modified Becke–Johnson (TB–mBJ) potential improves the band gaps over GGA and Engel-Vosko GGA. The computed TB–mBJ electronic band structure reveals that these materials are direct band gap insulators. The complex dielectric function of the metal oxyhalide compounds have been calculated and the observed prominent peaks are analyzed through the TB–mBJ electronic structures. By using the knowledge of complex dielectric function other important optical properties including absorption, reflectivity, refractive index and loss function have been obtained as a function of energy.

1. Introduction

Anti-perovskite compounds are of much scientific interest because of their versatile physical properties such as giant magneto resistance [1–5], nearly zero temperature coefficient of resistance [6]. Depending on the chemical composition, these materials can display variety of properties such as semiconducting, magnetic and super conducting properties. For example, magnesium based antiperovskites $AsNMg_3$, $SbNMg_3$ exhibit semiconducting properties. Recently the metallic behavior is also found in these materials due to the Mg vacancies [7–9]. Manganese based antiperovskite nitrides ($ANMn_3$, A = Ga, Zn, Cu) interplay a variety of magnetic properties and also exhibit the invar effect and nearly zero temperature coefficient of resistance [6,10]. $NiCMg_3$, $ZnCNi_3$, $CdCNi_3$ are well known superconductors [11–14]. In addition, high Young's modulus of antiperovskite Ti, Sc based anti-perovskite transition metal nitrides Ti_3AlN, Sc_3AlN made them good candidates for aero space applications [15–18].

In view of these important applications of antiperovskites it is worthwhile to know about their physical properties more in detail. Among the known antiperovskite compounds, the alkali metal oxyhalide compounds are relatively unexplored for their physical and chemical properties. Since the structures of these compounds contain unusual combinations of chemical elements it would be quite interesting to know their basic physical and chemical properties. Although these materials possess excellent electronic and bonding properties only few studies are available on these compounds in literature. The crystal structure of Na_3OCl was investigated by Hippler et al. [19] and found to be suitable candidate for determination of the Na^+ Sternheimer antishielding factor due to its cubic crystal symmetry [20,21]. The crystal structure and the related structural properties of K_3OBr were first reported by Sitta et al. [22]. The lattice dynamics and phonon spectrum of the compounds Na_3OCl, Na_3OBr, K_3OBr were studied using force constant method [23]. However, a number of basic properties of these compounds are still unknown. To the best of our knowledge there are no studies from experimental or theoretical side on the

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electronic, bonding, elastic, and optical properties of these compounds. The knowledge of electronic band structure and density of states is required to understand the conducting nature and the type of bonding present in the materials in terms of the band gap and the hybridization of different atomic states in the materials. They are also useful in understanding the various optical transitions that are possible. The optical properties, such as the absorption spectrum and the dielectric function, can be used to determine the optical band gap and dielectric constants, which are of fundamental importance in modeling the semiconducting devices. The other important physical properties of solids are mechanical properties. The mechanical properties of solids provide important information about the interatomic bonding and the type of forces present in the solids. The elastic constants are indispensable and are useful to know the mechanical behavior and stability of the solids. In this paper, we present a series of first-principles calculations on the structural, electronic, elastic, and optical properties of anti-perovskite alkali metal oxyhalides, Na_3OCl, Na_3OBr, and K_3OBr. The elastic constants and thereby different elastic moduli are calculated which are further used to discuss the mechanical behavior of the metal oxyhalides. The optical properties such as the dielectric function, reflectivity, absorption, refractive index and electron energy-loss function are calculated and discussed. The remainder of the paper is organized as follows. A brief description of methodology is given in Section 2. The results and discussion are presented in Section 3, followed by a brief conclusion in Section 4.

2. Computational details

The first principles calculations were carried out using two different density functional methods, plane wave pseudo-potential (PP-PW) method as implemented in CASTEP code [24,25] and full potential linearized augmented plane wave method (FP-LAPW) as incorporated in WIEN2k package [26]. For plane wave pseudo-potential calculations, we have used ultra-soft pseudo-potentials introduced by Vanderbilt [27] for treating the electron–nuclei interactions. The exchange–correlation (XC) functionals of Ceperley [28] and Alder parameterized by Perdew and Zunger (CA-PZ) [29,30] in local density approximation (LDA) and also the generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) [31] have been used for describing the electron–electron interactions. A plane wave basis set with kinetic energy cut-off of 410 eV for Na_3OCl, Na_3OBr and 420 for K_3OBr has been applied. For the Brillouin zone sampling, the $7 \times 7 \times 7$ Monkhorst–Pack [32] mesh has been used, in which the forces on the atoms are converged to less than 0.01 eV/Å and the total stress tensor is reduced to the order of 0.02 GPa.

In general, the standard DFT functionals LDA, GGA and Engel Vosko (EV)–GGA [33] usually underestimate the energy-band gap about 50% when compared to experiments as they suffer from artificial electron self-interaction and also due to the lack the derivative discontinuities of the exchange–correlation potential with respect to occupation number. In order to get reliable energy band gaps, one has to use more sophisticated methods such as hybrid functionals, GW approximation or TB–mBJ potential [34]. Among them, the later one produces an accurate energy band gaps almost comparable with experiments within a reasonable computation time. Therefore, the electronic structure and optical properties of the investigated compounds were calculated by using this TB–mBJ functional as implemented in WIEN2k package [26]. In order to achieve energy Eigen value convergence, the wave functions in the interstitial region were expanded in plane waves with a cutoff $K_{max} = 8/R_{MT}$, where R_{MT} is the smallest muffin-tin sphere while the charge density was Fourier expanded up to $G_{max} = 14$. The muffin-tin radii were considered to be 2.1, 2.3, 2.0, 2.5 and 2.6 atomic unit (a.u) for Na, K, O, Cl, and Br respectively. Self consistency was obtained using 35 k-points in the irreducible Brillouin zone (IBZ). The frequency dependent optical properties were calculated using dense k-points (286) in IBZ.

3. Results and discussion

3.1. Structural and elastic properties

As a first step, we performed the full structural optimization of the experimental crystal structure of the alkali metal oxyhalides within both LDA as well as GGA using PW-PP and FP-LAPW method within GGA. The calculated ground state properties such as lattice constants using two methods are in good accord with each other and found to be in excellent agreement with the experimental data [19,21,22]. Overall, from the calculated results we observe that the LDA values are underestimated by 2.7% and GGA values overestimated by 1.0%. This might be due to the inherent limitation of density functional theory (DFT) using LDA and GGA functionals. We fitted the total energy–volume data into third-order Birch–Murnaghan equation of state [35] to obtain the bulk modulus values of the compounds. The calculated equilibrium lattice parameters and bulk moduli using two different approaches are given in Table 1.

The elastic constants are fundamental and indispensable for describing the mechanical properties of materials. They also provide information about the mechanical, dynamical behavior and the nature of forces operating in solids, in addition to the mechanical stability and stiffness of materials. The elastic constants of the metal oxyhalides are calculated by applying a set of homogeneous deformations with a finite value and calculating the resultant stress with respect to optimizing the internal atomic coordinates. In general, there are 21 independent elastic constants (C_{ij}) required to describe the asymmetric crystal, but the symmetry of the cubic lattice reduces this number to only three independent elastic constants namely C_{11}, C_{12} and C_{44}. The mechanical stability criteria for a cubic crystal is, its three independent elastic constants should satisfy the following relations given by Born and Huang [36]:

Table 1
Calculated ground state lattice parameter ('a' in Å), bulk modulus (B, in GPa), elastic moduli (C_{ij}, in GPa), shear modulus (G_H, in GPa), Young's modulus (E, in GPa), anisotropy factor (A), Poisson's ratio (σ), and Cauchy's pressure (C_p, in GPa) of alkali oxyhalides Na_3OCl, Na_3OBr and K_3OBr. Experimental data are taken from Refs. [19,21,22].

Parameter	Method	XC	Na_3OCl	Na_3OBr	K_3OBr
a (Å)	PW-PP	LDA	4.381	4.450	4.986
		GGA	4.514	4.609	5.218
	FP-LAPW	GGA	4.543	4.613	5.282
	Expt		4.496	4.573	5.213
B (GPa)	PW-PP	LDA	41.3	39.4	27.1
		GGA	34.2	31.2	20.7
	FP-LAPW	GGA	32.5	31.1	19.9
C_{11} (GPa)	PW-PP	GGA	72.3	62.2	44.6
	FP-LAPW	GGA	68.5	62.1	41.6
C_{12} (GPa)	PW-PP	GGA	15.1	15.7	8.7
	FP-LAPW	GGA	14.4	15.8	7.6
C_{44} (GPa)	PW-PP	GGA	19.7	20.4	11.2
	FP-LAPW	GGA	19.0	19.8	10.6
G_H (GPa)	PW-PP	GGA	22.9	21.5	13.5
	FP-LAPW	GGA	21.9	21.1	12.8
G_H/B	PW-PP	GGA	0.67	0.69	0.65
	FP-LAPW	GGA	0.67	0.67	0.68
E (GPa)	PW-PP	GGA	56.2	52.5	33.3
	FP-LAPW	GGA	53.6	51.6	31.4
A	PW-PP	GGA	0.69	0.87	0.62
	FP-LAPW	GGA	0.70	0.86	0.62
σ	PW-PP	GGA	0.22	0.22	0.23
	FP-LAPW	GGA	0.22	0.22	0.22
C_P (GPa)	PW-PP	GGA	−4.60	−4.76	−2.37
	FP-LAPW	GGA	−4.60	−4.00	−3.00