Electronic and optical properties of alkali metal selenides in anti-CaF$_2$ crystal structure from first-principles

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ABSTRACT

We have performed FP-LAPW calculations in the framework of density functional theory (DFT) to compute ground-state electronic and optical properties of alkali metal selenides M$_2$Se [M: Li, Na, K, Rb] in anti-CaF$_2$ crystal structure. The generalized gradient approximation (GGA) parameterization schemes proposed by Wu and Cohen (WC) and Engel and Vosko (EV) have been utilized for these calculations and some trends in the electronic properties of alkali metal selenides have been analyzed in the light of available theoretical and experimental data of other group IA–VI crystals. Electronic density of states for these compounds has been obtained to elucidate contribution from different anion and cation states to the electronic structure. Optical properties such as complex dielectric function $\varepsilon(\omega)$, absorption coefficient $I(\omega)$, refractive index $n(\omega)$, extinction coefficient $k(\omega)$ and reflectivity $R(\omega)$ for incident photon energy up to 35 eV and energy-loss functions have been predicted for M$_2$Se compounds. Various interband transitions and the possible contributions of the cation and anion states to these transitions have been presented.

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1. Introduction

The oxides (M$_2$O) and chalcogenides (M$_2$Ch) of alkali metals [M: Li, Na, K, Rb; Ch: S, Se, Te] constitute a crystalline family that has shown great technological usefulness in devices requiring high ionic conductivity and large fundamental energy band gaps. Apart from being used in power sources, fuel cells, gas-detectors and ultra violet space technology devices, these ionic compounds also play important role in the development of photocathode, in supporting catalytic reactions and enhancing oxidation of semiconductor surfaces [1–8]. At room temperature these compounds crystallize into a stable anti-CaF$_2$ (anti-fluorite) structure type [9–10] (space group $Fm\bar{3}m$). The CaF$_2$ (calcium fluoride) compound has a basic crystalline structure that consists of a face-centered cubic packing of Ca cations, with F anions located in all the Ca tetrahedral. Whereas, the anti-morphous to the CaF$_2$ structure has exchanged positions of the cations and anions, and is known as the anti-fluorite type structure. In the M$_2$Se [M: Li, Na, K, Rb] compounds, the metal atoms (M) are located at (0.25; 0.25; 0.25) and (0.75; 0.75; 0.75) and the selenium atoms (Se) are located at (0; 0; 0) as shown in Fig. 1.

Unlike the oxide and sulfide compounds of this crystal family, the selenides of alkali metals have received less investigative attention from researchers towards their electronic and optical traits. Most of the research work for alkali metal selenides has been confined to studying the structural properties of these materials [11–14]. However, no theoretical and experimental account of the electronic and optical properties of these materials was available in literature until recently when Eithiraj et al. [15] utilized the Tight-Binding Linear Muffin-Tin Orbitals (TB-LMTO) method to investigate ground-state and under compression electronic behavior of selenides and tellurides of Li, Na and K.

In order to understand and enhance our knowledge of the electronic and optical properties of these materials and motivated by their inalienable importance among binary crystals, we have carried out self-consistent density functional calculations within the generalized gradient approximation (GGA) using the Full Potential Linearized Augmented Plane Wave (FP-LAPW) method. Calculated ground-state structural properties of the aforementioned crystals have been compared with available theoretical and experimental data. Moreover, features of the electronic band structures and optical parameters of alkali metal selenides have been analyzed in the light of available theoretical and experimental data of other group IA–VI crystals. The results for M$_2$Se compounds presented in this paper may provide reference for future experimental as well as theoretical studies related to these ionic materials and their intricate compounds.

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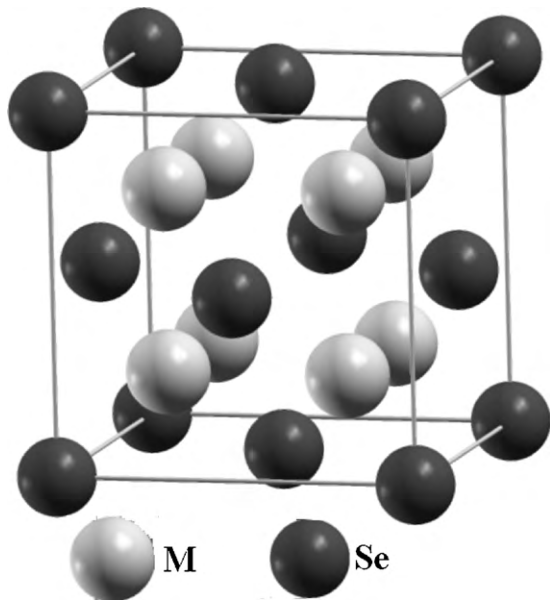   E-mail address: schaukat@gmail.com (A. Shaukat).

Fig. 1. Atomic structure of the anti-CaF$_2$-type M$_2$Se showing the face-centered cubic packing of (Se) anions, with (M) anions located in all the Se tetrahedral.

2. Calculational details and structural optimization

The density functional calculations for M$_2$Se ionic crystals were performed using the FP-LAPW method in the framework of density functional theory (DFT) as implemented in the WIEN2K code [16]. In these calculations, an approximate functional is required to determine the exchange-correlation energy (E_{xc}) whose accurate determination ensures the quality of obtained results. A crude determination of E_{xc} can be made with the local density approximation (LDA) [17] that can be readily calculated for a system consisting of homogeneous electron gas. However, in real crystalline solids such is not the case and the valence electron density being inhomogeneous in space, a refined determination of E_{xc} can

be achieved by using GGA exchange-correlation functionals. To this end the GGA expression proposed by Wu and Cohen [18] (WC) that performs fourth-order gradient expansion of exchange energy functional has proven most suitable for studying structural properties of solids as compared to the earlier GGA schemes such as the one devised by Perdew–Burke–Ernzerhof [19] (PBE). On the other hand, due to its simple form the WC functional is not flexible enough to accurately determine total exchange-correlation energy and its charge derivative. For this reason the modified GGA form of Engel and Vosko [20] (EV) GGA functional (that produces more accurate exchange-correlation potential at the expense of less accurate exchange energy) can be utilized; that has resulted in providing improved electronic band structure calculations for alkali metal oxides [21] and sulfides [22].

In the FP-LAPW method a muffin-tin model for crystal potential is assumed and the electrons are paired into two groups. The bound electrons have been treated as core electrons whose charge densities are confined within the muffin-tin spheres and the remaining are treated as valence electrons that reside outside the surface of muffin-tin spheres. The wave function, charge density and potential are expanded inside the non-overlapping spheres of muffin-tin radius (R_{MT}) around each species where linear combination of radial solution of the Kohn-Sham equation times the spherical harmonic has been utilized. Plane wave basis set has been utilized in the remaining interstitial space of the unit cell. The muffin-tin sphere radius, R_{MT}, for each species of the compounds under study is so chosen, that there is no charge leakage from the core and total energy convergence is ensured. The R_{MT} values for Li, Na, K, Rb and Se were selected to be 1.6, 2.1, 2.7, 2.9 and 2.8 a.u., respectively. These values have been selected after performing several tests using different muffin-tin radii as well as different sets of **k**-points to ensure convergence of energy. The maximum value of angular momentum ($\mathbf{l}_{max}$) for the wave function expansion inside the atomic spheres has been taken at 10. In the interstitial region the plane wave cut-off value of $\mathbf{K}_{max} \times R_{MT} = 9$ has been used for these calculations. A mesh of 72 **k**-points was taken for the Brillion zone integrations in the corresponding irreducible wedge.

Table 1
Lattice parameters a_o (Å), total energy E_0 (Ry), bulk moduli B_o (GPa) and its pressure derivative B' for alkali metal selenide. Results obtained in present work using WC GGA along with available experimental and theoretical values.

		Present work		TB-LMTO[g]	Other theoretical works
		WC GGA	Experimental		
Li$_2$Se	a_o	5.966	6.017[a,b]	6.030	–
	E_0	−4889.6890	–	−4885.1168	–
	B_o	34.7219	–	34.00	65[d], 35.1[e], 38.1[f]
	B'	3.8557	–	–	–
Na$_2$Se	a_o	6.796	6.823[a], 6.809[b]	6.755	–
	E_0	−5508.7397	–	−5502.8612	–
	B_o	24.8830	–	27.27	39[d], 22.6[e], 30.7[f]
	B'	4.1790	–	–	–
K$_2$Se	a_o	7.751	7.92[a], 7.676[b]	7.676	–
	E_0	−7266.9673	–	−7258.9557	–
	B_o	16.5313	–	18.64	24[d], 18.6[e], 21.6[f]
	B'	5.2240	–	–	–
Rb$_2$Se	a_o	7.984	8.02[c]	–	–
	E_0	−16,783.4194	–	–	–
	B_o	14.1218	–	–	–
	B'	3.7542	–	–	–

[a] Ref. [30].
[b] Ref. [9].
[c] Ref. [31].
[d] Ref. [13].
[e] Ref. [12].
[f] Ref. [14].
[g] Ref. [15].