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AB INITIO MODELING OF ALKALI METAL CHALCOGENIDES USING SOGGA THEORY

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ABSTRACT

The structural and electronic properties of some alkali metal chalcogenides namely Na_2Se, Na_2Te and K_2Te has been presented by employing the linear combination of atomic orbitals method. In the present study, the local density approximation, generalized gradient approximation and second order GGA formalism in the framework of density functional theory were used. The calculated lattice constant is in good agreement with the available experimental and theoretical data. Electronic properties are discussed from the calculations of band structure and density of states. The band structure calculations implies direct band gap with conduction band minima and valence band maxima at Γ point for Na_2Se and Na_2Te, whereas indirect gap is obtained for K_2Te.

Key words: Electronic band structure, Density functional theory, Wide band gap semiconductors, Alkali metal chalcogenides.

INTRODUCTION

The alkali metal chalcogenides with cubic anti-fluorite structure (space group No. 225)[1] have been extensively studied due to their high ionic conductivity and large band gaps. These compounds are promising candidates for the development of photocathode, fuel cells, solid state batteries, gas detectors and ultraviolet space technology devices. They have potential applications as power sources for portable electronic devices such as mobile phones, video cameras and notebook-type personal computers. They are also used in enhancing catalytic reactions and oxidation of semiconductor surfaces[2-5].

Recently, Ali et al.[6] have studied the structural, elastic, electronic, chemical bonding and optical properties of alkali metal selenides by first principles theory. The structural,

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phonon, thermodynamic and elastic properties of Na_2Te have been conducted by Zhang et al.[7] Kalarasse and Bennecer[8] have used the pseudopotential method to study the elastic, vibrational and dielectric properties of Na_2S, Na_2Se and Na_2Te. Several interesting properties of alkali metal chalcogenides have also been explored by full potential linearised augmented plane wave method[9-11]. Eithiraj et al.[12] have studied the electronic properties of alkali metal selenides and tellurides.

A lot of studies are devoted to the studies of alkali metal oxides and sulfides[13], but a very little work is undertaken to probe the properties of their selenides and tellurides. In this paper, we present the equilibrium lattice parameters, energy bands and density of states (DOS) of Na_2X (X = Se and Te) and K_2Te computed by using local density approximation (LDA), generalized gradient approximation (GGA) and second order GGA (SOGGA) theories of linear combination of atomic orbitals (LCAO) method as implemented in the CRYSTAL09 code of Torino group[14].

EXPERIMENTAL

Computational details

Ab initio methods have now become the most powerful probes for investigating important number of physical and chemical properties for atoms, molecules and solids. It uses the density of the valence electrons as a fundamental variable to calculate the ground state energies and related properties. In the LCAO approach, a linear combination of Gaussian orbitals is used to construct a localized atomic basis from which Bloch functions are constructed by a further linear combination with phase factors.

In density functional theory (DFT)[15-17], some approximations were applied to define the unknown exchange-correlation functional, E_{XC}, which describes the effects of the Pauli principle and the Coulomb potential beyond a pure electrostatic interaction of the electrons. The simplest is the LDA, where the E_{XC} term is a simple functional of the electron density and next is the GGA which uses also the gradient of the electron density to improve over LDA. In case of the DFT-LDA, we have used the exchange potential of VBH[18] and the correlation potentials of VWN[19], while for the DFT-GGA; the exchange and correlation potentials as prescribed by Perdew et al.[20] were implemented. Zhao and Truhlar[21] proposed modified PBE-type exchange functional, the so-called SOGGA functional; to recover the correct gradient expansion of slowly varying densities. It is called SOGGA because a second order density gradient expansion on the exchange enhancement factor is performed. This functional was developed to improve the lattice constants in solids.

In GGA, the E_{XC}^{GGA} for slowly varying densities is –

$$E_{XC}^{GGA} = \int n\,(r)\,\varepsilon_X^{LDA}\ [n\,(r)]\ F_X^{GGA}\ [s\,(r)]\ d^3r \qquad \ldots(1)$$

Where the reduced density gradient s(r) is represented as –

$$s(n(r)) = \frac{\nabla n(r)}{2k_F n(r)} \qquad \ldots(2)$$

and k_F is given by –

$$n(r) = \frac{k_F{}^3}{3\pi^2} \qquad \ldots(3)$$

The function $F_X^{GGA}[s(r)]$ is called the exchange enhancement function of the GGA and in the case of PBE, it is given by –

$$F_X^{PBE}(s) = 1 + K - \frac{K}{1 + \frac{\mu}{K}s^2} \qquad \ldots(4)$$

The constants used are $\mu = 0.2195$ and $K = 0.804$.

There is equal mixing of the PBE[20] and rPBE (revised PBE)[22] exchange functional of exchange enhancement factor for SOGGA approach, and it is given as –

$$F_X^{SOGGA}(s) = 1 + K\left(1 - \frac{1}{2}\frac{K}{1 + \frac{\mu}{K}s^2}\frac{1}{2}e^{-}\mu s^2/K)\right) \qquad \ldots(5)$$

For SOGGA, the values of the constants are redefined by using Lieb-Oxford bound[23], as $\mu = \mu^{GE} = 0.552$ and $K = 0.552$.

In these compounds, the metal atoms are located at (0.25; 0.25; 0.25) and (0.75; 0.75; 0.75) and the chalcogen atoms are located at (0; 0; 0). In present calculations, experimental lattice parameters used were 6.823Å, 7.329 Å and 8.168 Å for Na_2Se, Na_2Te and K_2Te, respectively[24]. The all-electron basis sets for Na, K, Se and Te were taken from http://www.tcm.phy.cam.ac.uk/~mdt26/basis_sets. Following the default tolerances in the CRYSTAL09 code, the SCF calculations have been performed for 120 k points in the irreducible Brillouin zone using Monkhorst-Pack shrinking factor of 15. Also, BROYDEN[25] scheme was used to achieve fast convergence.

RESULTS AND DISCUSSION

The equilibrium lattice constant *a* was calculated using DFT-LDA, GGA and SOGGA schemes. The obtained results are presented in Table 1 and are in reasonable agreement with the available theory and experiments. It can be seen that the calculated lattice constant using SOGGA theory is in better agreement with the experimental value, whereas the LDA and GGA approaches underestimates and overestimates the experimental data, respectively.

Table 1: Lattice parameter (*a*) and band gap (E_g) of Na_2Se, Na_2Te and K_2Te

		***a* (in Å)**			**E_g (in eV)**		
		Na_2Se	**Na_2Te**	**K_2Te**	**Na_2Se**	**Na_2Te**	**K_2Te**
Present Study	LDA	6.709	7.175	7.903	2.130	2.572	2.693
	GGA	6.894	7.366	8.198	2.151	2.622	3.982
	SOGGA	6.810	7.276	8.118	2.120	2.605	2.85
Previous theoretical studies	PBE[9]	6.856	7.383	8.237	2.09	2.11	1.98
	LDA[9]	6.651	7.107	7.919	1.92	1.98	2.06
	WCGGA[11]	6.796	7.285	8.114	1.99	2.01	2.25
	EVGGA[11]	-	-	-	2.98	2.96	2.88
	TBLMTO[12]	6.755	7.246	8.220	2.598	2.176	2.136
	VASP[25]	-	-	8.233	-	-	2.160
Previous Experiments	Anthony[24]	6.823	7.329	8.168	-	-	-
	Zintle et al.[26]	6.809	7.134	8.152			

In Figs. 1-3, the energy bands along with the DOS of Na_2S and Na_2Se and K_2Te have been shown, respectively using SOGGA theory. The energy is plotted in Hartree. Except for some fine structures and band gaps, the topology of our bands is in well agreement with previous studies[11,12]. In Table 1, we present the band gaps computed by using various schemes of LCAO method along with available data. As usual, the LDA theory underestimates and GGA approach overestimates the band gaps. From this table, one can infer that these calculations give lower value of band gap (for Na_2Se and Na_2Te) than those performed with the help of EVGGA[11] and TBLMTO[12] theories, while our computed data overestimates the results of PBE, LDA[9] and WCGGA approaches[11]. In the case of K_2Te, our data is comparable to WCGGA[11] theory and larger than all other reported data.

From the DOS figures, we can analyse the contribution of various cation and anion electronic states to the energy bands. The deep lying valence bands for Na_2X (X = Se and Te) (Figs. 1 and 2) are mainly due to *s* states of anion (Se and Te) atoms, which posses virtually flat character. The valence band width (VBW) has major contribution from the anion *p* states in both the compounds with small contributions from *s* and *p* like states of Na. In conduction band, mixing of electronic states of cation and anion atoms was found. In K_2Te (Fig. 4), the lowest bands around – 0.7 Hartree are mainly due to *p* states of potassium with small contribution from Te-*p* states. Then the lower and higher valence bands are dominated by Te *s* and *p* electronic states. The conduction bands have hybridization of *s*, *p* and *d* states of anion and cation. In Na_2X (X = Se and Te) compounds, the conduction band minimum (CBM) and the valence band maximum (VBM) occurs at Γ point, resulting in a direct band gap semiconductor, whereas, in the case of K_2Te, an indirect band gap exists, as the CBM lies at Γ point and the VBM at L point of the irreducible Brillion zone.

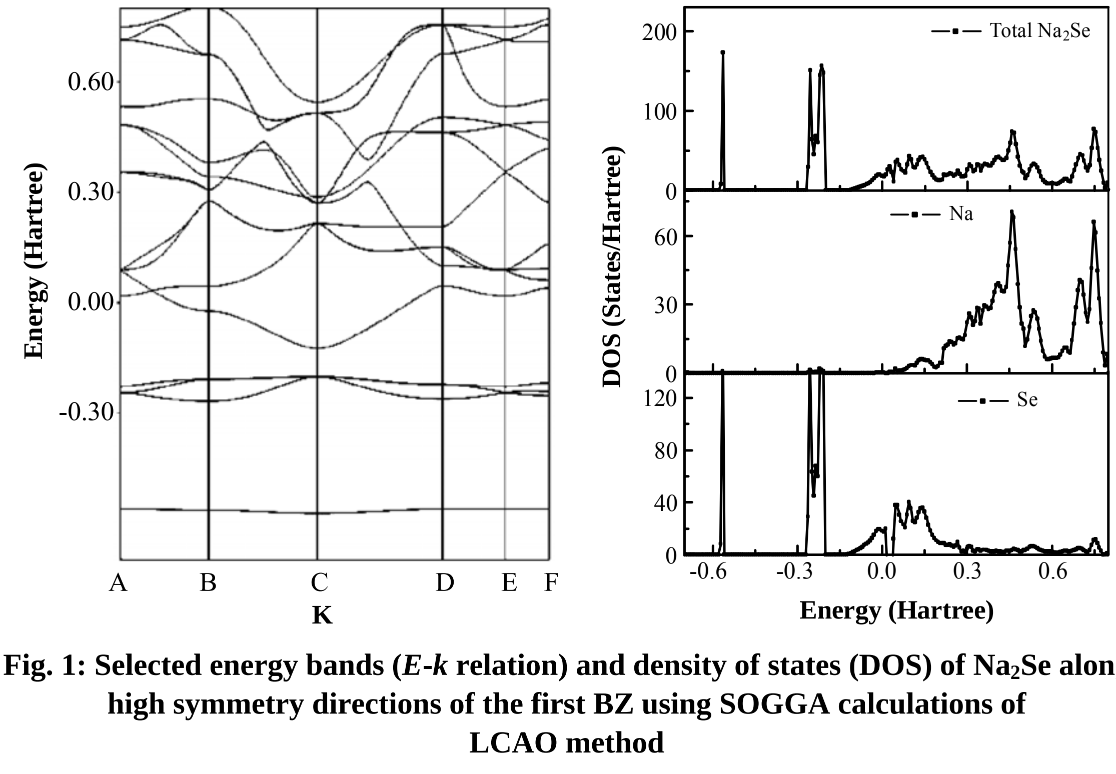

Fig. 1: Selected energy bands (*E*-*k* relation) and density of states (DOS) of Na_2Se along high symmetry directions of the first BZ using SOGGA calculations of LCAO method

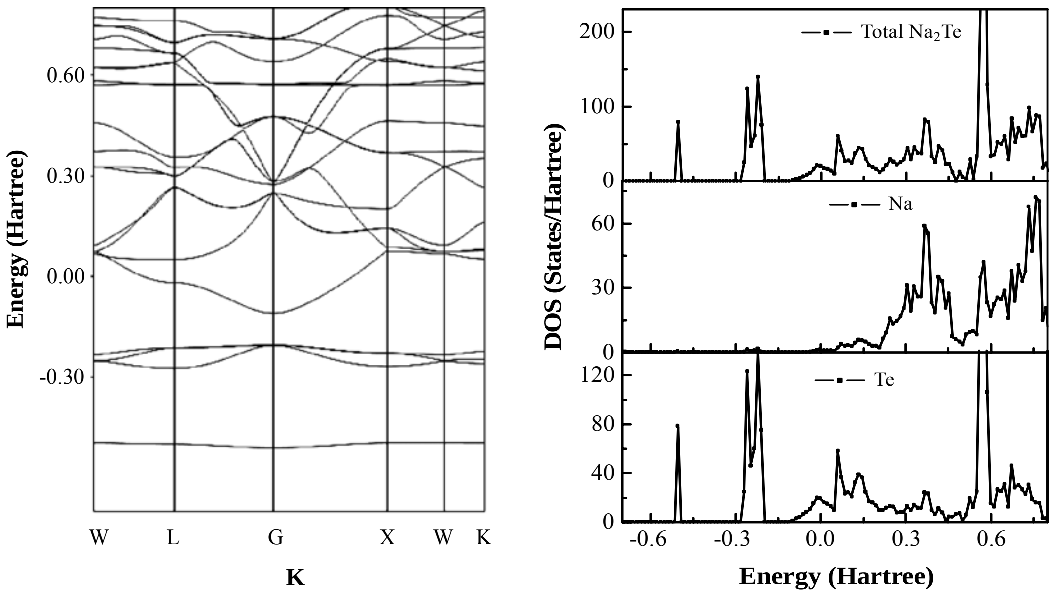

Fig. 2: Selected energy bands (*E-k* relation) and density of states (DOS) of Na_2Te along high symmetry directions of the first BZ using SOGGA calculations of LCAO method

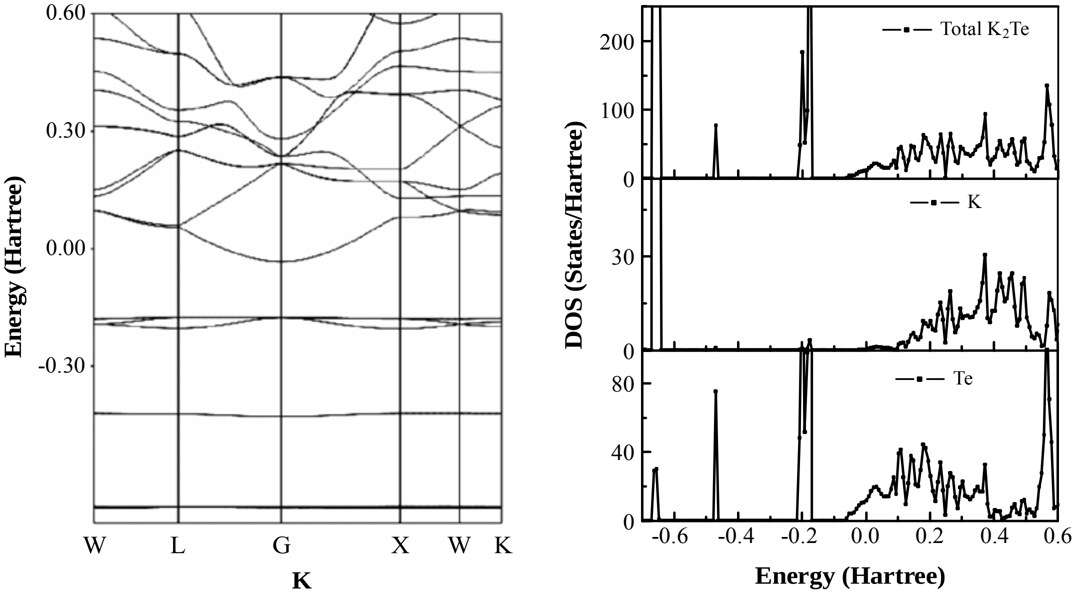

Fig. 3: Selected energy bands (*E-k* relation) and density of states (DOS) of K_2Te along high symmetry directions of the first BZ using SOGGA calculations of LCAO method

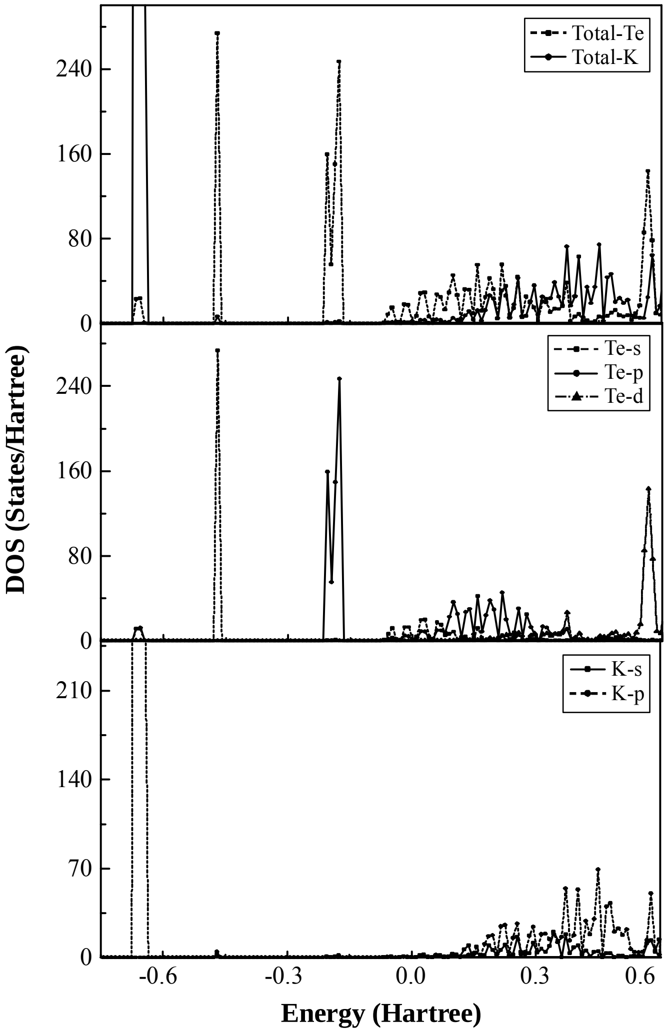

Fig. 4: Partial and total DOS of K and Te in K_2Te using SOGGA theory

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