

A Density Functional Approach to Study Alkali Metal Chalcogenides

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Abstract : The present work represents an ab initio study of structural, electronic and elastic properties of some Potassium Lithium Chalcogenides, KLiS and KLiSe using the local density approximation, generalised gradient approximation and hybrid approach of linear combination of atomic orbitals method. The paper includes calculations of lattice parameters and elastic constants C_{11} , C_{12} , C_{13} , C_{33} , C_{44} , and C_{66} of the chalcogenides. Also, the bulk modulus (B), shear modulus (G), Young's modulus (E) and Poisson's ratio (ν) have been evaluated. The results show that these compounds satisfy the mechanical stability criteria and exhibit brittle nature. The band structure calculations show that both the compounds possess indirect band gap.

Index Terms - Second Order Elastic Constants, Density Functional Theory, Alkali Metal Chalcogenide, Electronic Properties

I. INTRODUCTION

The ternary Potassium Lithium Chalcogenides, KLiX (X = S and Se) compounds crystallize in the anti-fluorite PbFCl-type tetragonal structure with space group no. 129 (P4/nmm) [1, 2]. In this crystal structure, the potassium atoms are located in the $2c$ (0.25, 0.25, ν), lithium atoms at $2a$ (0.75, 0.25, 0) positions and chalcogens S and Se take the $2c$ (0.25, 0.25, u) site. These materials exhibit anisotropic bonding nature. There are six independent elastic constants: C_{11} , C_{12} , C_{13} , C_{33} , C_{44} , and C_{66} to characterize tetragonal crystals. The structural, elastic and electronic properties of KLiS, KLiSe and KLiTe compounds have been determined by Seddik et al. [3] using full potential linearised augmented plane wave (FP-LAPW) method. Sabrowsky et al. [4] have studied the structural properties of KLiS, whereas Hippler et al. [5] have undertaken the structural study of KLiSe.

II. COMPUTATIONAL DETAILS

For determination of the structural, elastic and electronic properties of alkali metal chalcogenides, we have applied the second order generalized gradient approximation (SOGGA) scheme of LCAO method as embodied in CRYSTAL14 package [6]. In this scheme we solve the one electron Schrodinger's equation and calculate the crystal wave function. For this purpose, the Bloch orbitals of the crystal are expanded using atom-centered Gaussian orbitals of s, p or d symmetry and these crystalline orbitals serve as the solutions of the Schrodinger equation. In density functional approach (DFT), the exchange and correlation potential operator can be expressed in terms of exchange correlation density functional energy E_{xc} and the electron density ρ at a point r as:

$$\hat{v}_{xc}(r) = \frac{\delta E_{xc}\{n(r)\}}{\delta \rho(r)} \quad (1)$$

To evaluate structural parameters, band structure and elastic properties of KLiS, we have used the exchange function of Zhag and Truhlar [7] and correlation potentials of Perdew et al. [8] under SOGGA scheme, while for KLiSe, we have implemented the PBEsol approach [9]. The exchange enhancement function for SOGGA theory, $F_X^{SOGGA}[s(r)]$, is obtained by equal mixing of the PBE [8] and rPBE [10] (revised PBE) exchange functional of exchange enhancement factor and can be written as,

$$F_X^{SOGGA}(s) = 1 + \kappa \left(1 - \frac{1}{2} \frac{\kappa}{1 + \frac{\kappa}{s^2}} - \frac{1}{2} e^{-\mu s^2/\kappa} \right) \quad (2)$$

The constants are chosen as $\mu = \mu^{GE} = 0.552$ and $\kappa = 0.552$ using Lieb-Oxford bound [11]. The Gaussian basis sets for K, Li, S and Se have been used [12] to compute the structural and elastic properties of KLiX. In addition, the BRODYEN scheme [13] has been used for faster convergence of self consistent-field cycles. The elastic constants calculations have been performed by using the method of Perger et al. [14].

III. RESULTS AND DISCUSSION

3.1 Structural and electronic properties

The equilibrium structural parameters, like, lattice parameters a , c and atomic fractional coordinates u , ν for KLiS and KLiSe have been computed by applying geometry optimization method. In Table 1, we have presented the present data along with the previously reported theory and experimental values. Our computed lattice parameters and fractional coordinates are in good agreement with the theoretical [3] and experimental [4, 5] values.

The electronic band structure and electronic density of states (DOS) for KLiS and KLiSe have been plotted along some high symmetric directions in the first Brillouin zone (BZ) at equilibrium volume and shown in Figure 1 and 2, respectively. We have plotted the energy scale in Hartree (a.u.). Except for some fine structures and band gaps, the overall shape of our energy bands is in

agreement with the earlier reported data [3]. Both the compounds show indirect band gap with valence band maximum at Z point and the conduction band minimum at the Γ point of the irreducible BZ.

Table 1 Structural properties of KLiS and KLiSe using SOGGA and PBEsol methods of LCAO.

Structural parameters (\AA)	KLiS			KLiSe		
	Present Study SOGGA	Previous Work		Present Study PBEsol	Previous Work	
		WC-GGA [3]	Experiment [4]		WC-GGA [3]	Experiment [5]
<i>a</i>	4.283	4.276	4.317	4.490	4.462	4.517
<i>c</i>	6.888	6.920	6.962	6.844	7.189	7.241
<i>u</i>	0.1896	0.1887	0.1905	0.1960	0.1920	0.1996
<i>v</i>	0.6522	0.6590	0.6587	0.6674	0.6623	0.6453

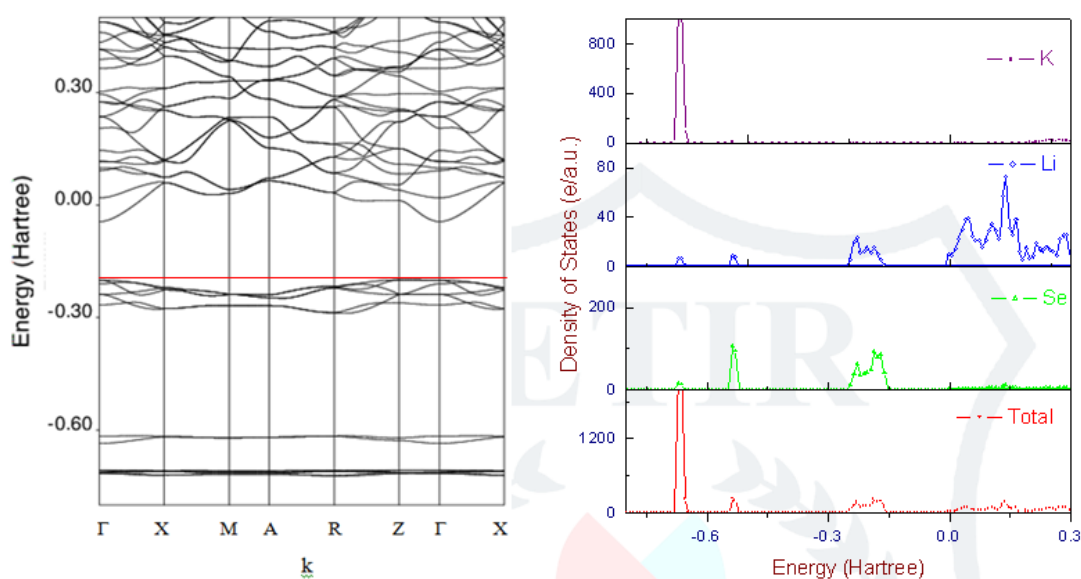


Fig. 1 The energy bands and density of states of KLiS computed using DFT-SOGGA scheme of LCAO theory.

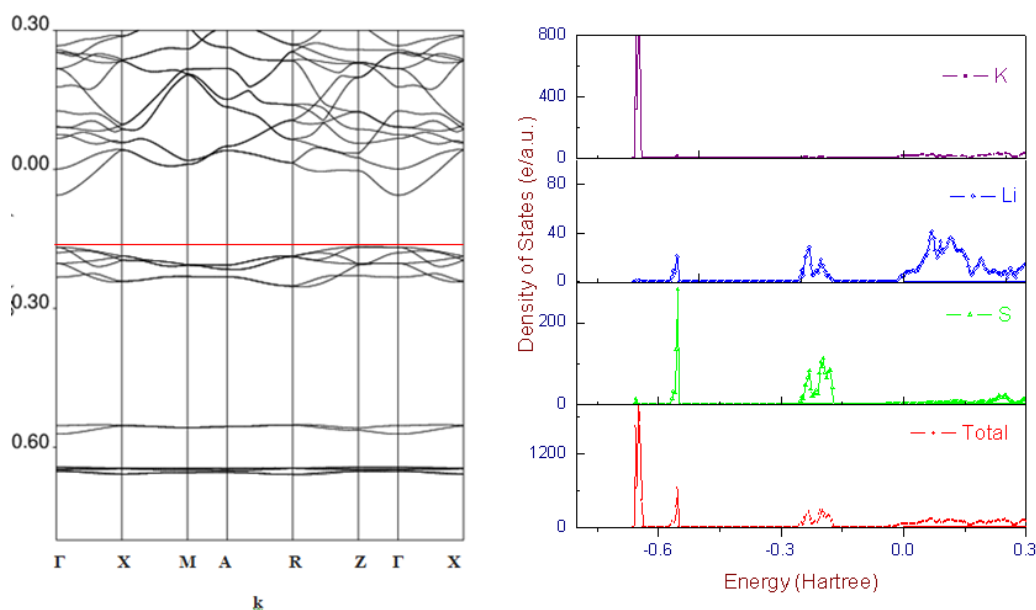


Fig. 2 The energy bands and density of states of KLiSe computed using DFT-GGA (PBEsol) scheme of LCAO theory.

The computed band gaps for KLiX are shown in Table 2. The DOS curves show the contribution of alkali metals and chalcogen atoms in the formation of energy bands. For example, in the case of KLiSe (in Fig. 2), the lowest valence bands are dominated by p states of K atom. The top of the VB are formed by contribution due to Se-p states and Li-s and -p electronic states. The conduction band is mainly due to K-d states, Li- s, -p states and Se-p, -d states.

3.2 Elastic and Mechanical properties

In cubic tetragonal crystals, $C_{11} = C_{22} \neq C_{33}$, and their difference reflects in terms of anisotropic properties of mechanical moduli. The mechanical stability of compounds can be easily checked from elastic constant values as presented below:

$$C_{11} > 0; C_{33} > 0; C_{44} > 0; C_{66} > 0; (C_{11} - C_{12}) > 0; (C_{11} + C_{33} - 2C_{13}) > 0; [2(C_{11} + C_{12}) + C_{33} + 4C_{13}] > 0 \quad (3)$$

The calculated elastic constants C_{ij} are presented in Table 2, which satisfy the mechanical stability criteria as described in Eq. (3). Hence the two compounds studied are intrinsically stable. The polycrystalline Young's modulus (E) and the Poisson's ratio (ν) have been computed as follows,

$$E = 9BG / (3B + G) \quad (4) \nu$$

$$= (3B_H - 2G_H) / 2 * (3B_H + G_H) \quad (5)$$

Table 2 Elastic and Electronic Properties of KLiS and KLiSe

	KLiS		KLiSe	
	Present Study	Previous Work	Present Study	Previous Work
Elastic Constants (GPa)	SOGGA	WC-GGA [3]	PBEsol	WC-GGA [3]
C_{11}	67.38	63.88	54.35	54.41
C_{12}	10.61	12.69	15.29	10.66
C_{13}	21.92	20.16	19.57	17.65
C_{33}	54.72	43.12	51.23	37.43
C_{44}	16.90	16.64	16.46	14.72
C_{66}	28.21	38.77	24.97	32.58
Shear Modulus B	38.31	30.53	29.86	26.30
Bulk Modulus G	22.39	20.78	18.34	17.88
B/G	1.599	1.469	1.628	1.47
Young's Modulus E	56.22	50.81	45.67	43.73
Poisson's Ratio ν	0.26	0.22	0.25	0.22
Energy Gap (eV)	3.034	3.295 4.297 (EVGGA)	4.092	2.710 3.645 (EVGGA)

Our computed mechanical properties agree well with the WCGGA calculations of Seddik et al. [3]. The value of B/G is directly related to plastic properties of materials and it has a critical value of 1.75. If its value is less than 1.75 the compound shows brittleness, otherwise ductile nature [15]. Table 2 clearly proves the brittle character of both the compounds. Also the value of Poisson's ratio gives insight to the nature of crystal. With $\nu < 0.26$, the material exhibits brittle character and here the two compounds studied have the value of ν lying between 0.22 and 0.26, hence in agreement with the B/G condition for brittleness.

IV. CONCLUSIONS

The present work includes computations of structural, electronic and elastic properties first time using the linear combination of atomic orbitals method. We found that the alkali metal chalcogenides studied have indirect band gaps with valence band maxima at Z point and conduction band minima at Γ point. The materials are mechanically stable and possess a brittle nature.

V. ACKNOWLEDGMENT

The authors are grateful to Prof. R. Dovesi for providing the CRYSTAL14 package.

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