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# Structural and Elastic Properties of KLIS

Physics

**KEYWORDS :** Band Structural Calculations; Matlockite Compounds; Density Functional Theory

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## ABSTRACT

*-Structural, electronic and elastic properties of the tetragonal alkali metal chalcogenides KLiX [X: S, Se and Te] have been investigated using the full-potential (linearized) augmented plane wave plus local orbitals method. The exchange–correlation potential is treated within the generalized gradient approximation of Wu and Cohen. Moreover, the alternative form of GGA proposed by Engel and Vosko is also used for the electronic properties. The calculated Structural parameters are in excellent agreement with the experimental data. The elastic constants Cij are predicted using the total energy variation versus strain technique. The polycrystalline elastic moduli, namely; shear modulus, Young's modulus, Poisson's ratio, sound velocities and Debye temperature are derived from the obtained single-crystal elastic constants. Brittleness behavior of these compounds is interpreted via the calculated elastic constants Cij. Calculated band structures show that KLiS and KLiSe have an indirect energy band gap, whereas KLiTe has a direct energy band gap. The contribution of alkali metals and chalcogen atoms to the electronic band structure and electronic density of states has been analyzed. This is the first quantitative theoretical prediction of the elastic and electronic properties for these investigated compounds and still awaits experimental confirmations.*

## 1. INTRODUCTION

During the recent past years, theoretical methods have becomeone of the fields of the most active research in physics of matter. It involves using the ab initio methods to comfortably give, for example, an interpretation of experimental spectra and to predict (electronic, mechanical, and optical) properties of new materials. Ternary alkali metal chalcogenides with the general formula ABX, where A and B represent different alkali metals (Li, Na, K, Rb and Cs) and X is a chalcogen (O, S, Se and Te), have attracted the interest of materials researchers. The first studied inter alkali metal chalcogenides were KNaO and RbNaO. Indeed, in 1982, Sabrowsky and Schröer [1] elaborated and characterized these later compounds and confirmed their tetragonal anti-PbFCl-type structure. Later on, Sabrowsky and co-workers [2–5] have explored others inter alkali metal chalcogenides such as KLiX where X = S, Se, Te. It was noticed that these materials adopt a tetragonal anti-PbFCltype structure with space group P4/nmm (#129). The alkali metalatoms K and Li are located in the Wyckoff sites 2c (1/4, 1/4,zK) and 2a (3/4, 1/4, 0), respectively, while the chalcogen atom occupies the Wyckoff site 2c (1/4, 1/4, zch), where $z_K$ and $z_{ch}$ are the internal structure parameters describing the positions of K and chalcogen atoms along the z-axe. The KLiX compounds (X = S, Se, Te) have been less explored. To the best of our knowledge, apart from the structural properties, experimental and theoretical data on KLiX are scarce. Neither experimental nor theoretical details regarding the electronic and elastic properties are available for a purpose of comparison.

The KLiX chalcogens are beautiful examples of mixed ionic and covalent type materials. Herein, a strong ionic character arises in the K-(S, Se and Te) bonding and a covalent Li-(S, Se and Te) bonding as a consequence of the chalcogen "p"-like states with Li "s" and "p"-like states hybridization. Due to the lack of structural and electronic structure information relevant to the KLiX compounds, a time tested strategy is to study the systematics using

the full-potential (linear) augmented plane-wave plus local orbitals method (FP-L/APW + lo), based on the first-principles density functional theory (DFT). These are predictive results for the first time on the structural, electronic and elastic properties and need detailed investigations on these materials. The rest of the paper 0927-0256/$has been divided in three parts. In Section 2, we briefly describe the computational method used in this study. The most relevant results obtained for the structural, elastic and electronic properties of the KLiX compounds are presented and discussed in Section 3. Finally, we summarize the main conclusions in Section 4.

### Computational method

The present calculations were performed by means of the full-potential method with mixed basis APW + lo (LAPW) [14,15] implemented in Wien2K computer code [16]. The exchange and correlation effects were treated by following the Wu and Cohen generalized gradient approximation (GGA-WC) [17]. In addition, for the electronic band structure the Engel–Vosko (EVGGA) scheme [18] was applied. The latter approximation is used to overcome the shortcoming of the underestimation of the energy gaps in both LDA and GGA [19,20]. This shortcoming is ascribed to the fact that LDA and GGA do not reproduce the exchange correlation energy and its charge derivative correctly. The plane-waves cut-off was used with the condition RMTKmax. = 7,

where RMT is the smallest muffin-tin sphere radius and Kmax. is being the largest k vector in the plane wave's expansion. The muffin-tin sphere radius was chosen to be 2.5, 2.26, 2.26, 2.46 and 2.54 a.u. for K, Li, S, Se, and Te, respectively.

The electronic configurations $4s^1$ for K, $2s^1$ for Li, $3s^2 3p^4$ for S,$3d^{10} 4s^2 4p^4$ for Se and $4d^{10} 5s^2 5p^4$ for Te were chosen as valence states. The k-point sampling in the Brillouin zone (BZ) was treated by using the Monkhorst–Pack scheme [21] with an 11 × 11× 7 grid which corresponds to 82 irreducible points in the first BZ. The self-consistent calculations were considered to be converged when the difference in the total energy of the crystal did not exceed 10_4 Ryd. as calculated at consecutive steps. During the calculation of band structure and density of states (DOSs), a dense k-grid of 18 ×18 × 11 is used which corresponds to 270 irreducible k points.

### Structural properties

The crystalline structure of KLiX (X = S, Se, Te) is characterized by three free parameters: the lattice constant a, internal structure parameters (zK and zch) and the ratio c/a. We have performed two sets of calculations. As a first step, starting from the experimental lattice parameters, we have optimized the internal parameters by relaxing the z-coordinates of the potassium and chalcogen atoms until the forces on the ions were below a tolerance value taken as 0.001 eV/Å. Second, using the optimized internal parameters, the total energy is calculated at different volumes V and c/a ratio

values, to obtain the absolute minimum in total energy for each structure. The calculated total energies versus volumes were fitted to the Murnaghan equation of state [14] in order to obtain the structural parameters; namely, the equilibrium volume (V0) of the unit cell, lattice constants, a and c, bulk modulus B as well as its first pressure derivative B'. Deduced results are presented in Table 1, which also contains experimental data for comparison.

Our computed lattice parameters a, c and c/a ratio as well as the optimized internal parameters (zK and zch) are in good agreement with the available experimental data. We note that the calculated lattice constant values are slightly lower than the measured ones while the GGA is generally known by its slight overestimation of the lattice constan value. This discrepancy is probably due to the measurement conditions, such as the accuracy of measurement, temperature of measurement and so on. Some researchers have reported that the calculated lattice constant values using GGA-WC functional which are slightly underestimated compared to the measured ones (see for example Refs. [15–18]). In view of Table 1, it is clear that the calculated bulk modulus value decreases from KLiS to KLiTe, suggesting that the compressibility increases from KLiS to KLiTe. Henceforth, the lattice parameter enlargement and the reduction in bulk modulus indicate the softening tendency of lattice on increasing size of chalcogens. We note that the potassium and lithium atoms are the same in the three compounds, so the chalcogen S, Se and Te atoms size could be the responsible for the lattice constant increasing from KLiS to KLiTe.

**Table 1**
**Theoretical and experimental lattice constants (in Å), internal structural parameters and, bulk moduli (in GPa) and their pressure derivatives of the tetragonal KLiS, KLiSe and KLiTe compounds**

| System | $a_0$ | c0 | c/a | $z_K$ | $z_{ch}$ | $B_0$ | $B_0$ |
|---|---|---|---|---|---|---|---|
| KLiS<br>This work | 4.2757 | 6.920 | 1.618 | 0.6590 | 0.1887 | 31.60 | 4.42 |
| Expt.a | 4.3179 | 6.962 | 1.612 | 0.6587 | 0.1905 | - | - |
| KLiSe<br>This work | 4.462 | 7.189 | 1.611 | 0.6623 | 0.1920 | 26.74 | 4.30 |
| Expt.b | 4.517 | 7.241 | 1.603 | 0.6453 | 0.1996 | - | - |
| KLiTe<br>This work | 4.784 | 7.639 | 1.596 | 0.6685 | 0.1995 | 21.37 | |
| Expt.c,d | 4.839 | 7.717 | 1.596 | 0.670 | 0.2056 | - | - |
| | 4.83 | 7.704 | 1.595 | 0.66387 | 0.2 | - | - |

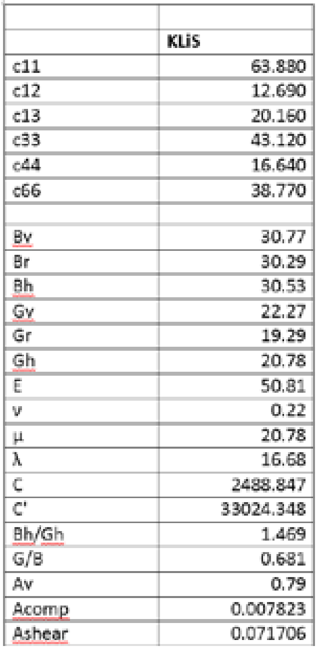
## Elastic constants and their related properties

In the present work, we have usedthe local density approximation (LDA), generalized gradient approximation (GGA), second order GGA (SOGGA) and hybridization of HF and DFT, so called B3LYP approaches as embodied in CRYSTAL09 package [22] of Torino group, Italy. In case of the DFT-LDA computation, the exchange potential of VBH [23] and the correlation potentials of VWN [24] have been adopted while for the DFT-GGA, the exchange and correlation potentials as prescribed by Perdew et al. [25] were implemented. We have also employed the SOGGA theory, as this functional approximates structural properties of solids accurately.

The measurement of the elastic properties using the SOGGA functional has not previously been done. It is named 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. For SOGGA, the exchange function of Zhag and Truhlar [26] and correlation potentials of Perdew et al. [27] were considered. In the B3LYP, the exchange correlation density functional energy involves the Becke's gradient correction [28] to the exchange and correlation functionals using prescription of Lee–Yang–Parr [29]. To compute the structural and elastic properties of BaFCl we have used Gaussian basis sets for Ba, F, and Cl from http://www.tcm.phy.cam.ac.uk/~mdt26/basis_sets. To obtain the elastic constants for the tetragonal BaFCl, the change of total energy with lattice deformation was evaluated by the theory ofPerger et al. [30]. In matlockite structure, the F ions occupy the Wyckoff positions 2*a* but the Ba and Cl atoms are at the positions 2*c* which depend on the internal parameters *u* and *v*.

**Table-2**
**DATA ANALYSIS OF KLiS**



| | |
|---|---|
| | KLiS |
| c11 | 63.880 |
| c12 | 12.690 |
| c13 | 20.160 |
| c33 | 43.120 |
| c44 | 16.640 |
| c66 | 38.770 |
| | |
| Bv | 30.77 |
| Br | 30.29 |
| Bh | 30.53 |
| Gv | 22.27 |
| Gr | 19.29 |
| Gh | 20.78 |
| E | 50.81 |
| v | 0.22 |
| µ | 20.78 |
| λ | 16.68 |
| C | 2488.847 |
| C' | 33024.348 |
| Bh/Gh | 1.469 |
| G/B | 0.681 |
| Av | 0.79 |
| Acomp | 0.007823 |
| Ashear | 0.071706 |

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