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Lithium halide monolayers: Structural, electronic and optical properties by first principles study

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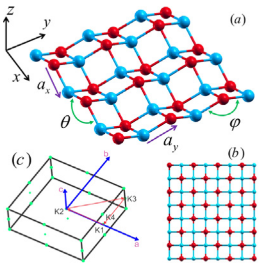
HIGHLIGHTS

- Structural optimizing represents that unlike graphene-like structures, the cubic face structure is more favorable for alkali halide 2D structures.
- Nonbonding electron pairs cause a planar buckling for all compounds.
- Electronic calculations show that all compounds have an indirect energy gap.
- All compounds are optically transparent in the visible spectrum range.

GRAPHICAL ABSTRACT



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ABSTRACT

Using first principle study, we investigate the structural, electronic and optical properties of lithium halide monolayers (LiF, LiCl, LiBr). In contrast to graphene and other graphene-like structures that form hexagonal rings in plane, these compounds can form and stabilize in cubic shape interestingly. The type of band structure in these insulators is identified as indirect type and ionic nature of their bonds are illustrated as well. The optical properties demonstrate extremely transparent feature for them as a result of wide band gap in the visible range; also their electron transitions are indicated for achieving a better vision on the absorption mechanism in these kinds of monolayers.

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1. Introduction

Alkali halides known as ionic compounds are characterized by their highly crystalline nature, high melting points and strong miscibility in polar media [1,2]. These materials can be considered as prototype insulator materials with great technological importance [3–5]. For many years, thermodynamic, elastic, structural and electronic properties of them have been investigated comprehensively. The effect of defects in these compounds has been presented too [6,7]. Also band structure investigations reveal these compounds are recognized as wide-gap insulators that demonstrate their optical transparency in the visible region of the electromagnetic spectrum [8]. This transparency feature, especially in LiF, in high compression makes this material a suitable choice for versatile window material through which to carry out wave profile measurements for shock compression experiments [9]. These compounds generally crystallize in both B1 (NaCl-type) and B2 (CsCl-type) structures. Their phase transitions have been classified as pressure and temperature dependence in first-order kind [7,10]. On the other hand, studying the role of electronic correlation on the boundary between localized and delocalized electronic states become possible through energy level investigation, due to their electronic states kind. Their applications for a range of optical applications are significant besides the interaction mechanisms between the electronic and geometric structure can

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be interestingly demonstrated [11]. LiF, LiCl and LiBr, known as Li halides, have been investigated in bulk phase theoretically [12–14] and experimentally [15,16]. As a result, the energy difference between the top of the valence band and the outermost core levels in LiF, LiCl and LiBr was determined by the electron spectroscopy for chemical analysis (ESCA) technique in the bulk phase. The energy differences obtained between the top of the valence band and the Li 1 s line in LiF, LiCl and LiBr were 49.8 eV, 53.2 eV and 54.1 eV respectively. These results agree rather well with the predictions of the point charge model, including corrections for polarization effects [15]. Since there has been increased attention to the properties of thin films and nanostructures, the great theoretical interest was paid to their nanostructures due to interest in the application of alkali halide systems as sensitive photostimulable storage materials [17]. Low dimensional alkali halide nanocrystals of LiF were investigated structurally and energetically by Bichoutskaia and Pyper in 2006 [18]. The required energy for forming one plane of new contacts in the LiF ($2\times2\times n$) chain is essentially constant and independent of the lengths of the two fragments being joined. Also the simulation performed with density functional theory (DFT) and coupled-cluster (CCSD) calculations on the series of $(\mathrm{LiF})_{n=2,36}$ neutral clusters showed that nanotube structures with hexagonal and octagonal transverse cross-sections are stabile, and this stability is similar to the typical cubic form of large LiF crystals [19]. These investigations showed that these Li halides in cubic shape have been formed regardless to cross section of nanostructures. Here we focus on Li halide monolayers in structural, electronic and optical aspects to achieve a point of view in these kinds of nanostructures for the first time. Our preferable structure for investigation is cubic structure agreed with previous researches mentioned above.

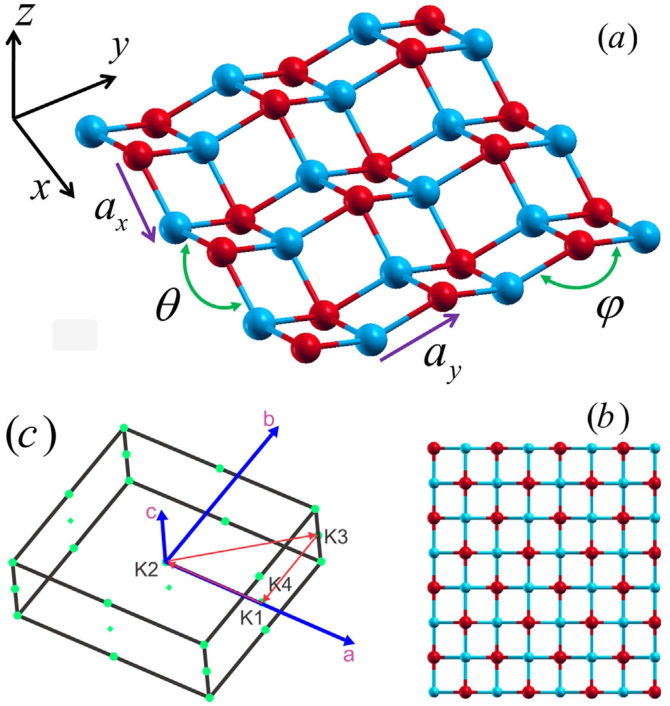

Fig. 1. Lithium halide monolayer: (a) length bond illustrated for x- and y-directions and different angles created by structural optimizing, (b) top-view of monolayer and (c) first Brillouin zone with k-path for energy band structure calculations.

2. Computational details

In order to calculate our results, the first principles study in the framework of the density functional theory [20,21] as implemented in WIEN2k code [22] is used. To achieve reliable results we have performed full potential augmented plane waves plus local orbitals (FPAPW+lo). The generalized gradient approximation energy functional formulated by Perdew–Burke–Ernzerhof (GGA-PBE) [23] has employed as the approximation method for the exchange–correlation energy functional. The cut-off parameter known as $R_{MT}\ K_{max}$ that it has been equaled 7, the value of this parameter demonstrates our accuracy and efficiency and $G_{max}=14\ \mathrm{Ry}^{1/2}$ as another parameter of charge calculations. The optical data of this paper has been performed by using the random phase approximation (RPA) method [24] to gain imaginary part of dielectric function and Kramers–Kronig relations for real part. The number of k-points is 5000 in the first Brillouin zone that leads to $24\times22\times8$ as a good mesh for calculations here.

3. Results and discussion

In order to explain electronic and optical characteristics of LiF, LiCl and LiBr monolayers, this part is required to achieve the best configuration to find balance situation in structures and reach acceptable results.

3.1. Structural investigation

In order to find stable configurations of these monolayers energetically, we have optimized volume as implemented in Birch–Murnaghan equation of state [25] and relax these structures to get closer to minimum force possible exerting to each atom. The structural optimization results express that the cubic face for these ionic compounds is more preferable than the other configurations, and these results demonstrate good agreement with previous calculations for alkali halide nanotubes [19]. In Fig. 1a, stable structure of these monolayers as a representation of Li halides has been illustrated for better understanding. Fig. 1b is the top-view of these monolayers. The first Brillouin zone for these kinds of structures is shown as well (see Fig. 1c). The optimized parameters, i.e. bond length, buckling factor and angle between each three close atoms in each direction are presented in Table 1 for LiBr, LiCl and LiF. These parameters are identified in Fig. 1 to find the distinction of these variables in these monolayers.

It is obvious that these two dimensional structures are not flat and get planar buckling after relaxation set. This phenomenon occurs as a result of the existence of nonbonding electrons in halogen atoms. In the other words, after bond formation, three pairs of nonbonding electrons have broadened in a side and push the other bonding orbital to another side, so this monolayer get buckled naturally. When we investigate a 2D monolayer, these nonbonding electrons located on opposite sides in adjacent atoms to achieve structural stability. Thus buckling formation in these monolayer is a natural reformation.

3.2. Electronic properties

In order to show the bond nature of these structures, electron

Table 1
The measured angle of every three atoms in the x-direction (θ) and y-direction (ϕ), bond length of structure in the x-direction (a_x), bond length of structure in the y-direction (a_y) buckling factor for all of under discussion compounds.

Compounds	θ (degr)	ϕ (degr)	a_x (Å)	a_y (Å)	Δ
LiF	136.15	160.60	1.88	1.92	0.70
LiCl	132.10	151.41	2.41	2.51	0.97
LiBr	132.16	147.01	2.57	2.70	1.04

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