IIETA International Information and Engineering Technology Association
Advancing the World of Information and Engineering

Annales de Chimie - Science des Matériaux
Vol. 44, No. 6, December, 2020, pp. 413-419
Journal homepage: http://iieta.org/journals/acsm

Theoretical Investigation of Structural and Optoelectronic Properties of Ternary Acetylides A_2MC_2 (A = Li, Na, K) and (M = Te, Pb, Pt)

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https://doi.org/10.18280/acsm.440607

Received: 29 September 2020
Accepted: 26 November 2020

Keywords:
theoretical study, density functional theory, optoelectronic properties, material engineering, material characterization, ternary acetylides

ABSTRACT

In this work, the structural and optoelectronic parameters of the ternary bialkali acetylides A_2MC_2 (A = Li, Na, K) and (M = Te, Pd, Pt) with trigonal structures are investigated. The study is conducted by using the first-principles pseudo-potential plane-wave technique, which is based on the Density Functional Theory (DFT) and integrated in the CASTEP software. A special attention is paid to the Tellurium based compounds, since they are less studied. A satisfactory agreement is reported between our results of the structural parameters and those of the literature. Predictions are performed to determine the values of the band gaps and optical parameters.

1. INTRODUCTION

The ternary bialkali acetylides A_2MC_2 are very interesting materials. During few decades, many research works have been conducted on these materials in the field of inorganic chemistry [1-5]. In general, these materials may be synthetized by employing solid-state reaction of parent A_2C_2 with considered metal M at high temperature [6-8]. Many compounds were synthetized involving Rb, K, Na, and Cs alkali metals and Pt and Pd transition metals [1, 2, 4, 7, 9-11]. Terdik et al. [12] predicted that the photo-emissive properties of Cs_2Te may be enhanced by adding an acetylenic unit to obtain the Cs_2TeC_2 compound. Therefore, related materials like the Li_2TeC_2 may have the same photo-emissive characteristics. Recently, tellurium based ternary acetylides Li_2TeC_2 (Na_2TeC_2) were synthetized for the first time by Németh et al. [13]. They obtained these compounds after synthetizing Li_2C_2 (Na_2C_2) by reacting the elemental Li (Na) with acetylene gas. New materials with distinct structures and different properties have been updated by Głodek et al. [14], Chan et al. [15], Svahn et al. [16], Marmol et al. [17], and Sanchez-de-Diego et al. [18], using multiple diagnostic techniques. On the other hand, there are many fields of use of these structures in several areas, as shown by Lankelma et al. [19], Tian et al. [20], Kuroda et al. [21], Hau et al. [22], and Zhou et al. [23].

2. PURPOSE

The aim of this work is to inspect the structural and optoelectronic characteristics of the A_2MC_2 (A = Li, Na, K) and (M = Te, Pb, Pt) family. The study is based on the density functional theory. The CASTEP software is used as a tool to perform the calculations.

3. COMPUTATIONAL METHOD

The first-principles pseudo-potential plane-wave technique, which is based on the Density Functional Theory (DFT) and integrated in the CASTEP software was used in our calculations [24].

The generalized gradient approximation of Perdew et al. [25] was utilized to ensure the exchange-correlation functional. The Monkhorst-Pack technique [26] was adopted to integrate the special points sampling over the Brillouin zone. Meshes with 8×8×8 *k*-point were considered. 360 eV was the energy selected value of cut-off. The minimization approach of Broyden-Fletcher-Golfarb-Shanno (BFGS) was utilized to determine the structural parameters [27].

4. FINDINGS AND DISCUSSION

4.1 Structural characteristics

The ternary acetylides compounds A_2MC_2 are known to crystallize in a trigonal structure with space group (P3m1, 164) (Figure 1). These compounds are characterized by atomic fractional coordinates (zA, zC) and lattice parameters (a, c).

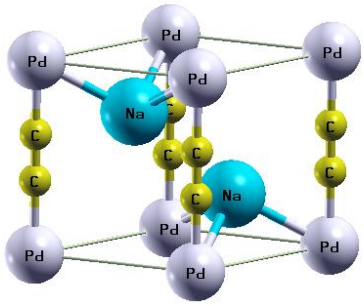


Figure 1. Trigonal structure of ternary acetylides compounds A_2MC_2

Table 1. (*a* and c), B, and E_g for the A_2MC_2 compounds

	Lattice constant *a (Å)*		Lattice constant *c (Å)*		Bulk Modulus *B (GPa)*		Energy Gap E_g *(eV)*	
	This work	Exp.	This work	Exp.	This work	Exp.	This work	Exp.
Li_2TeC_2	4.25	-	6.00	-	45.12	-	1.448	-
Li_2PdC_2	3.85	-	5.30	-	11.28	-	0.243	-
Li_2PtC_2	3.98	-	5.26	-	44.68	-	0.094	-
Na_2TeC_2	4.79	-	6.16	-	9.69	-	1.737	-
Na_2PdC_2	4.55	4.464[1]	5.32	5.266[1]	26.89	-	0.997	-
Na_2PtC_2	4.64	4.503[1]	5.27	5.205[1]	27.14	-	0.507	-
K_2TeC_2	5.19	-	6.11	-	26.85	-	2.244	-
K_2PdC_2	5.13	5.105[2]	5.32	5.282[2]	23.12	-	1.591	-
K_2PtC_2	5.18	5.123[2]	5.28	5.218[2]	65.81	-	1.129	-

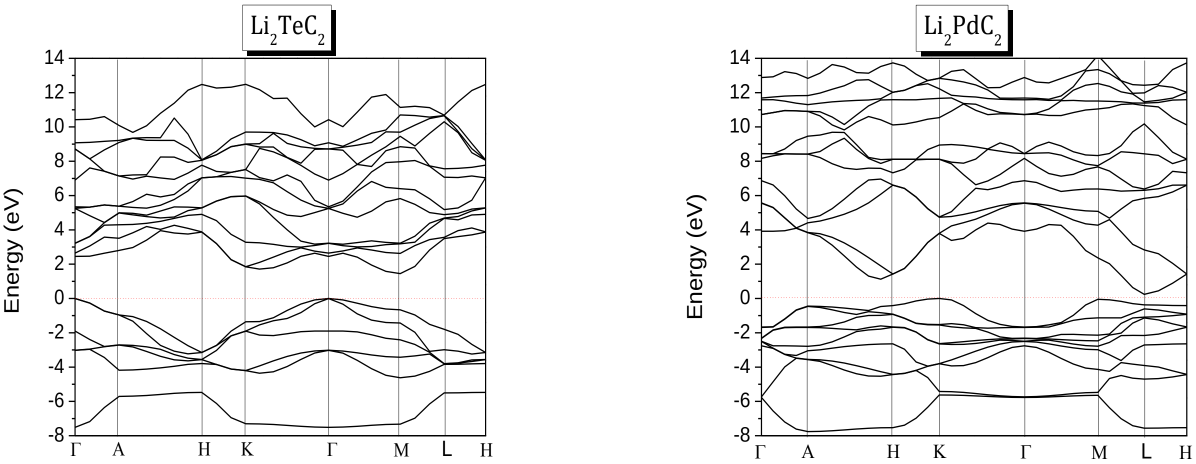
Note: (1): Ref. [6]; (2): Ref. [8].

Table 1 summarises the values of the parameters *a* and c. It reports a comparison between our findings and the available experimental data. As clearly remarked, both results are in good agreement. In the knowledge of authors, no experimental results for the bulk modulus or its pressure derivative are available in the literature.

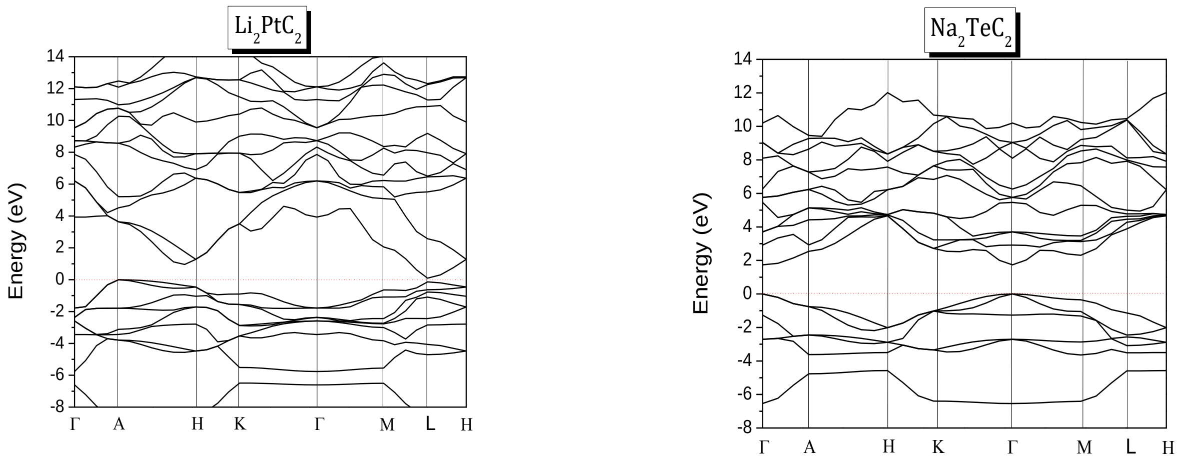
4.2 Electronic characteristics

The structures of the energy band of the investigated compounds are shown in Figure 2. Our results are predictions, since no experimental details are found in the literature for the band gap of these compounds. It is seen from Figure 2 that for Te-based compounds, Na_2TeC_2 and K_2TeC_2 present G-G direct gaps of 1.737 and 2.244 eV respectively while Li_2TeC_2 is G-M indirect gap of 1.448 eV.

The band gaps are all A-L indirect except for Li_2PdC_2 which is K-L one. The partial and global density of states of Li_2TeC_2 and Li_2PdC_2 are shown in Figure 3, which reveals the existence of upper valence bands consisting of Te-p and C-p orbitals located before the Fermi level for Li_2TeC_2, while for Li_2PdC_2 the orbitals are Pd-p and C-p. The same behavior is seen for the others but the upper valence bands consist of Pd-d or Pt-d and C-p orbitals. For the latters, the strong hybridization between Pd-d or Pt-d and C-p states in the upper valence band shows a covalent bonding character.

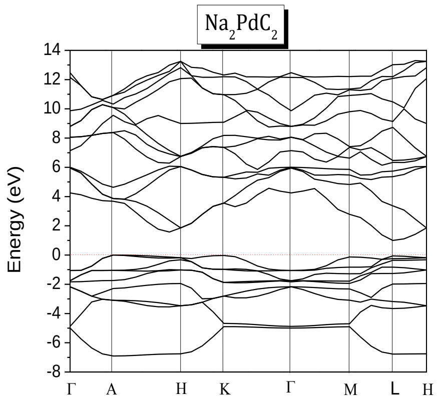


(a) Li_2TeC_2 (b) Li_2PdC_2

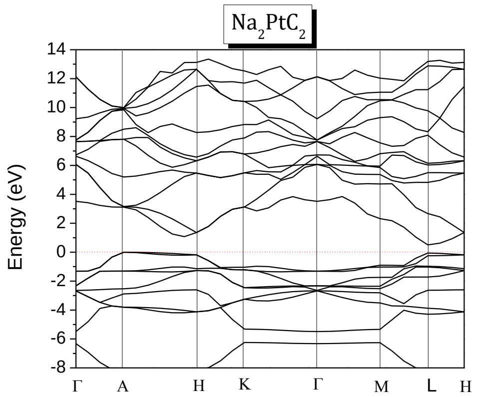


(c) Li_2PtC_2 (d) Na_2TeC_2

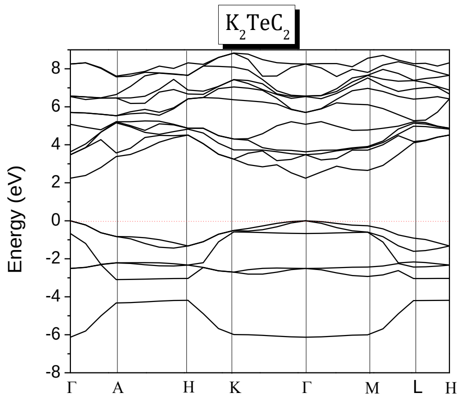
(e) Na_2PdC_2



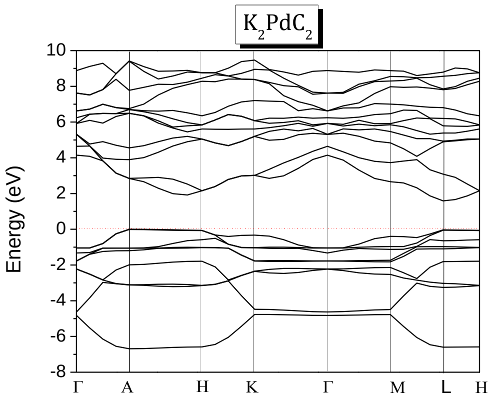
(f) Na_2PtC_2



(g) K_2TeC_2



(h) K_2PdC_2



(i) K_2PtC_2

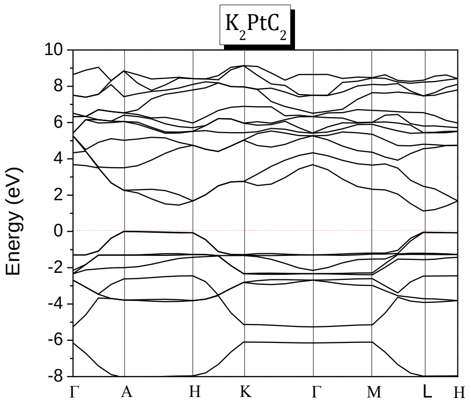
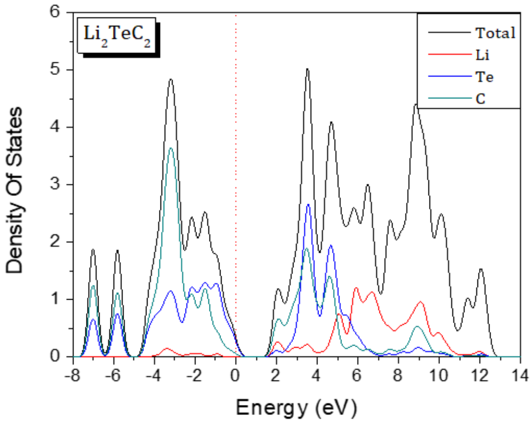
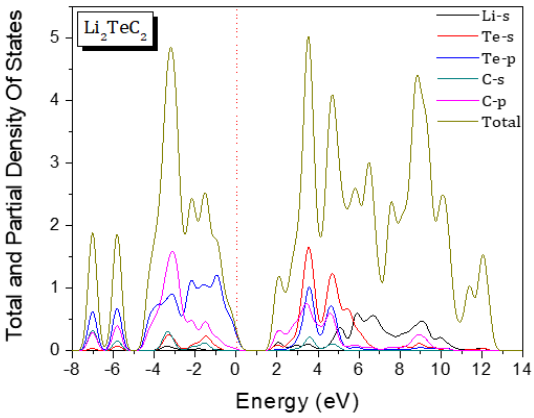


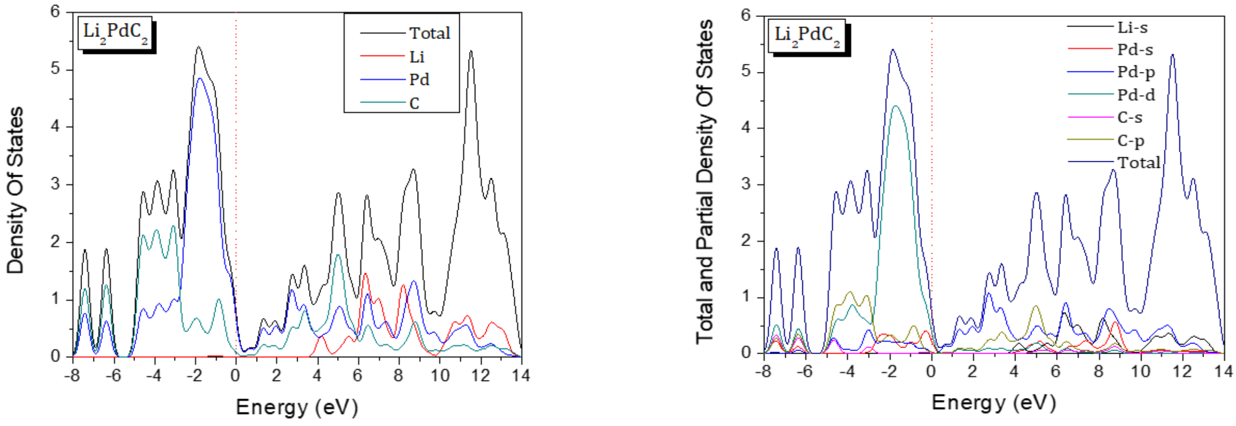
Figure 2. Band Structures of the investigated A_2MC_2 compounds

(a) Density of states (Li_2TeC_2)



(b) Total and partial density of states (Li_2TeC_2)




(c) Density of states (Li_2PdC_2)

(d) Total and partial density of states (Li_2PdC_2)

Figure 3. Partial and global density of states of Li_2TeC_2 and Li_2PdC_2 compounds

4.3 Optical properties

The real (dispersive) and imaginary (absorptive) parts of the dielectric functions for the investigated compounds as function of the photon energy are shown in Figure 4.

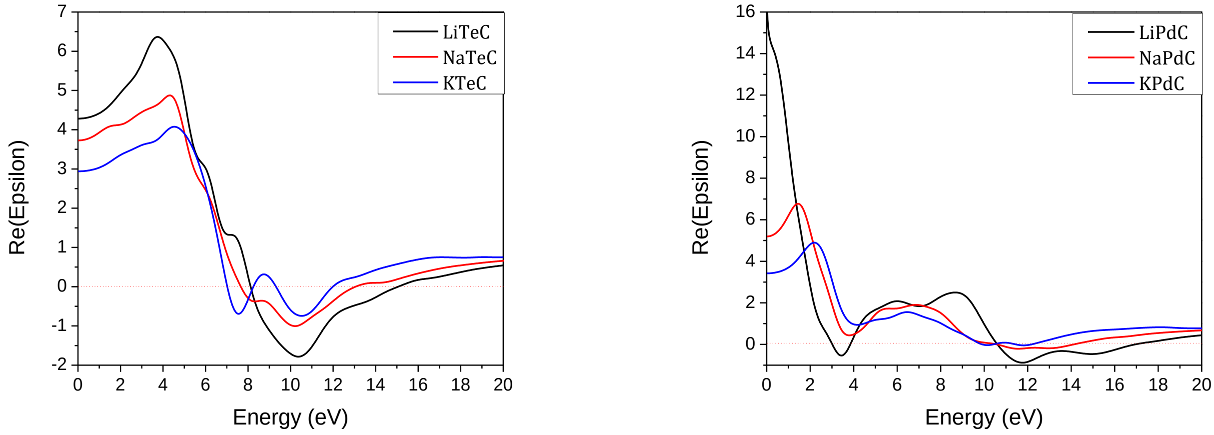
The static dielectric constants ε (0) for Li_2TeC_2, Na_2TeC_2 and K_2TeC_2 are respectively 4.28, 3.73, and 2.94 and reach the peaks at about 3.73, 4.32 and 4.5 eV. For Li_2PdC_2, Na_2PdC_2 and K_2PdC_2, the ε (0) values are 16.62, 5.19, and 3.42 respectively.

While for Li_2PtC_2, Na_2PtC_2 and K_2PtC_2, the static dielectric constants ε (0) are respectively 10.17, 5.07, and 3.48 eV and reach their maxima at 0.88, 1.72 and 2.61 eV.

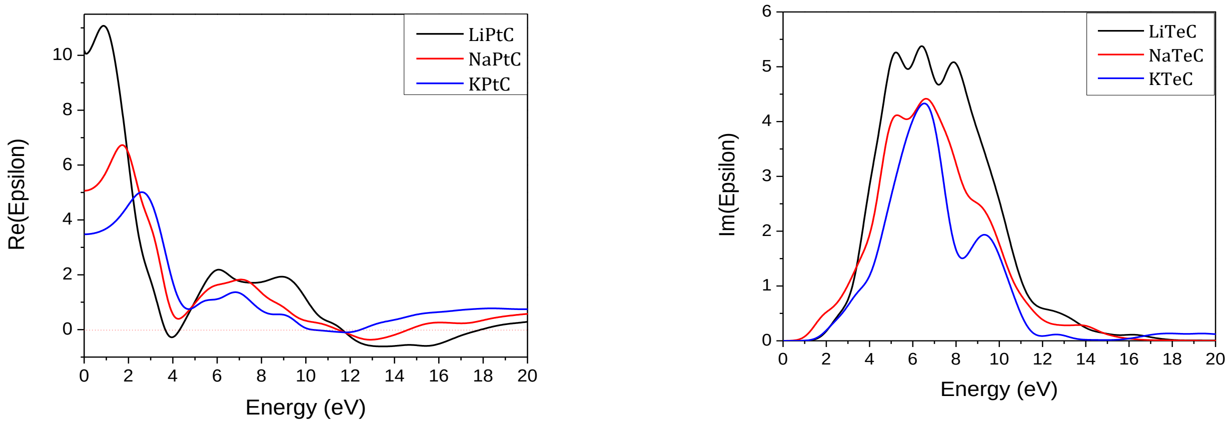
The absorptive part is mainly characterized by the broad peak. The transitions from the valence to the conduction bands are given by the peaks of the dielectric functions.

The maximum mounts of the peak for Li_2TeC_2, Na_2TeC_2 and K_2TeC_2 are respectively at 6.43, 6.62, and 6.54 eV.

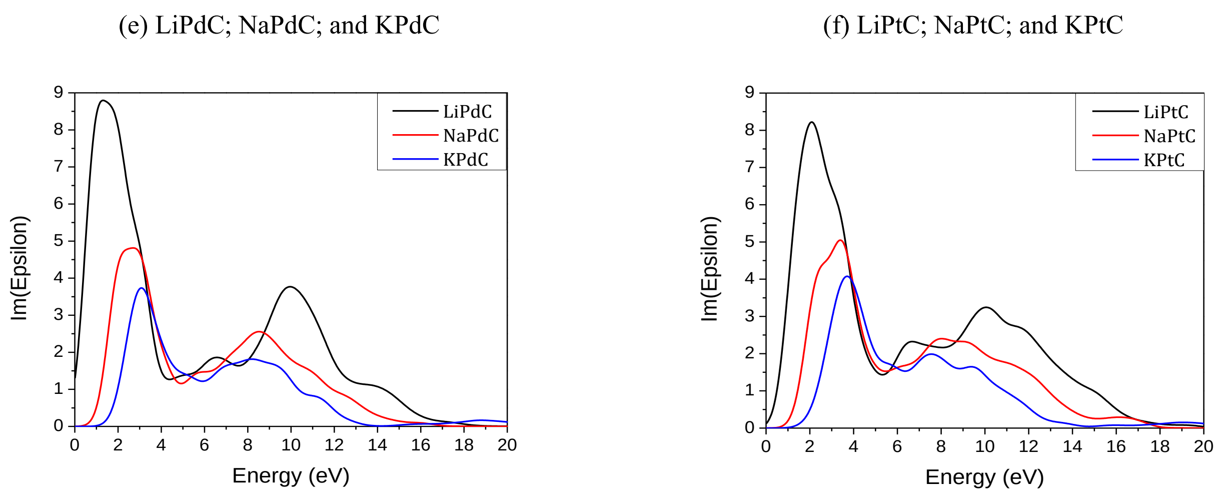
For Li_2PdC_2, Na_2PdC_2 and K_2PdC_2, the peaks are at 1.32, 2.70 and 3.10 eV respectively, while for Li_2PtC_2, Na_2PtC_2 and K_2PtC_2, they are respectively at 2.08, 5.07, and 3.40 eV.


(a) LiTeC; NaTeC; and KTeC

(b) LiPdC; NaPdC; and KPdC


(c) LiPtC; NaPtC; and KPtC

(d) LiTeC; NaTeC; and KTeC


(e) LiPdC; NaPdC; and KPdC

(f) LiPtC; NaPtC; and KPtC

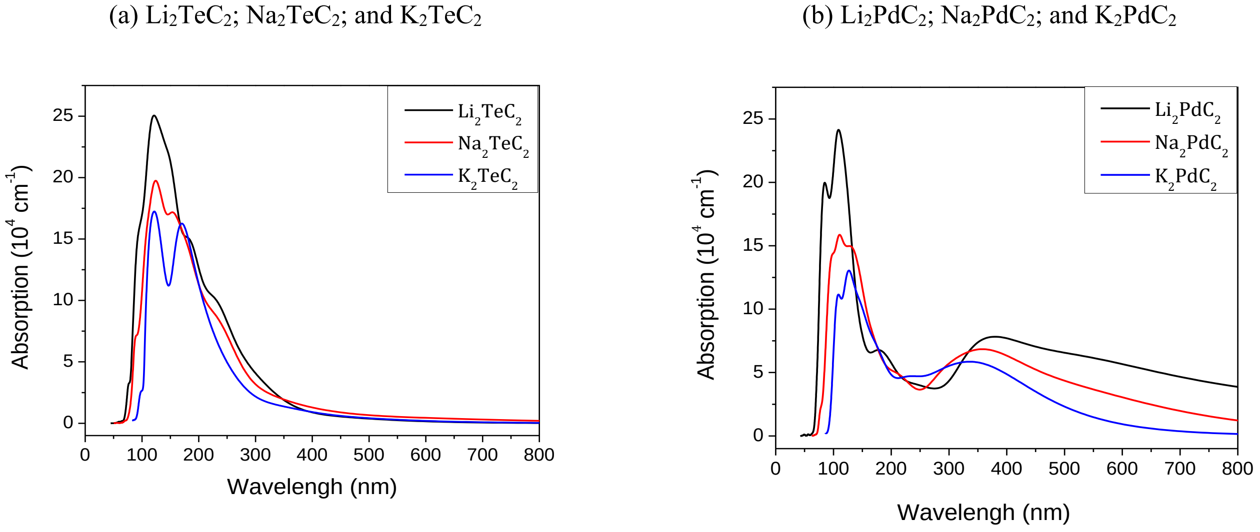
Figure 4. Imaginary and real parts of the dielectric function of the investigated A_2MC_2 compounds

Figure 5 illustrates the absorption spectra of the studied materials, which are relatively similar and present significant absorption bands between 60 and 150 nm, but for Te-based compounds the absorption band is shifted up to 250nm. When plotting the absorption spectra of the studied compounds versus energy, we noticed that optical absorption of Li-based materials starts respectively from very low E.

Note that:

(i) a maximum absorption corresponds to a maximum conduction and to a minimum dispersion,

(ii) a minimum value of the real part of the dielectric function.


(a) Li_2TeC_2; Na_2TeC_2; and K_2TeC_2

(b) Li_2PdC_2; Na_2PdC_2; and K_2PdC_2

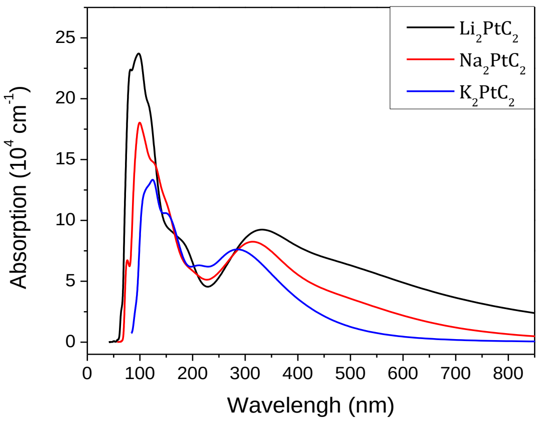

(c) Li_2PtC_2; Na_2PtC_2; and K_2PtC_2

Figure 5. Absorption spectra of the investigated A_2MC_2 compounds

5. CONCLUSION

The opto-electronic and structural, characteristics of Te, Pd and Pt based alkali acetylides namely A_2MC_2 (A = Li, Na, K) and (M = Te, Pd, Pt).

The investigation has been carried out by utilizing the pseudo-potential plane-wave technique that is based on the theory of the density functional density. The generalized gradient approximation has been also adopted. The structural parameters were in satisfactory agreement with the available experimental findings. The energy gaps and optical parameters are predicted. The Te-based compounds present higher gap values. The investigated materials also show band absorption situated in the ultra-violet region.

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