

Theoretical calculations for MUO₃ (M = Na; K; Rb): DFT + U studySikander Azam^a, A.H. Reshak^{a,b,*}^a New Technologies – Research Center, University of West Bohemia, Univerzitni 8, 306 14 Pilsen, Czech Republic^b Center of Excellence Geopolymer and Green Technology, School of Material Engineering, University Malaysia Perlis, 01007 Kangar, Perlis, Malaysia

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ABSTRACT

The energy band structure, density of states and electronic charge density for MUO₃ (M = Na; K; Rb) compound has been inspected in support of density functional theory (DFT). We have employed the GGA + U to treat the exchange correlation potential by solving Kohn–Sham equations. It is well known that density functional theory underestimates band gaps of materials which have highly localized valence electrons. On the other hand, the predictions of electronic properties of materials, which do not have localized band near the band gap, by DFT are not accurate enough as well. The effect of electronic correlation on properties of MUO₃ (M = Na; K; Rb) compound is theoretically studied in this paper. The calculations show that the investigated compounds are semiconductor with direct/indirect energy gap of about 4.466, 4.652 and 4.326 eV for NaUO₃, KUO₃ and RbUO₃, respectively. The density of states expresses that valence band is mostly dominated by U-s/p/f and O-p states. While the conduction band is composed of U-f/d and Na/K/Rb-s/p orbitals. Covalent bond is formed between U and O atoms as can be seen from PDOS that U-p and O-d states hybridized around –0.2. The linear optical properties were also discussed in particular.

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Introduction

The actinide components have got much attention due to magnetic and optical properties. With the theoretical calculations the 5f components can become extremely complicated due to the comparable magnitudes of the crystal field, the electron–electron repulsion interactions and the spin–orbit coupling.

The studies for the series of compounds like MUO₃ (M = alkaline cation) has been explored [1–15], for the reason that they enclose uranium in the U(V) valence state, which has the electronic configuration [Rn]5f¹. It makes the situation simpler, with the reason that there are no electron–electron repulsions to take into description.

Despite the big amount of crystallographic, chemical and thermodynamic data available, the selective information of the rather intricate uranium ternary oxides is yet away from complete. One of the key topics is the localized structure around the uranium ions and accordingly their accurate oxidation state in diverse compounds [16]. Complications with ascribing valences in uranium mixtures have been accounted [17] for KUO₃, RbUO₃, and NaUO₃.

Legally, these structures comprise only one uranium valence, namely U⁺⁵.

The crystal structures of these compounds are based on a perovskite structure with only one crystallographic position for U. In so far as these two observations tend, no objection is found in categorizing these materials as pure monovalent compounds. However, from the previous study it has been reported that the X-ray photoelectron spectroscopy (XPS) spectra of these uranates expose doublet structures for the U4f peaks [18,19], which can be inferred as a mark of a mixed valence state. The X-ray absorption fine structure (XAFS) spectroscopy is an organized method to local environment of actinides in their compounds [19]. XAFS has been classified in to two regions: Extended X-ray absorption fine structure (EXAFS), and X-ray absorption near edge structure (XANES) [20].

The purpose of this work is to theoretically tune the electronic correlation (and exchange) to predict the energy band structure, density of states, electronic charge density and optical properties for MUO₃ (M = Na; K; Rb) compound. We have found that, it is not mainly the lack of correlation, rather than the lack of proper attractive interaction (“negative correlation”) in the orbitals that is responsible for the poor results of MUO₃ (M = Na; K; Rb) by the traditional DFT. To demonstrate this, here, we have employed DFT + U approach in calculating the energy band structure, density of states and electronic charge density for MUO₃ (M = Na; K; Rb)

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compound. The goal is to improve all of these properties simultaneously. A major issue with DFT + U method is to find an appropriate U-value for a particular material, especially for materials which has not been traditionally studied with DFT + U. In general, the U-parameter can be determined self-consistently by a linear response method [29]. Here we have followed the latter approach to systematically study the effect of electronic correlation term U on MUO_3 ($M = Na; K; Rb$) in an unconventional way.

Method of calculations

The MUO_3 ($M = K, Rb$) crystallizes in the cubic space group $pm\bar{3}m$ while the $NaUO_3$ compound is crystallizes in orthorhombic symmetry having space group $pbnm$. The unit cell structure for the three compounds have been shown in Fig. 1. The crystallographic data has been taken from the work of Berghe et al. [21], the lattice

constants and the atomic positions for the three compounds are specified in Table 1. The calculations for the present compounds have been carried out with a full potential linear augmented plane wave (FP-LAPW) method [22], this is because of the new and the more recent articles by the K. M. Wong et al. [23,24] on the first-principles studies using the DFT based FP-LAPW method as implemented in the WIEN2k code for the study of the electronic properties of materials as substantiated in WIEN2K code [25]. Using the GGA [26], the electronic exchange correlation functions were treated. As it is well known that GGA approximation overestimate the band gap. In order to overcome the well-known underestimated band gap problem of the uranium mixtures including 6d and 5f electrons, the GGA + U correction [27] was adopted to treat the outer 6d and 5f electrons of the uranium. By using GGA + U method, the underestimation of the intraband Coulomb interactions is corrected by the Hubbard U parameter. The physical

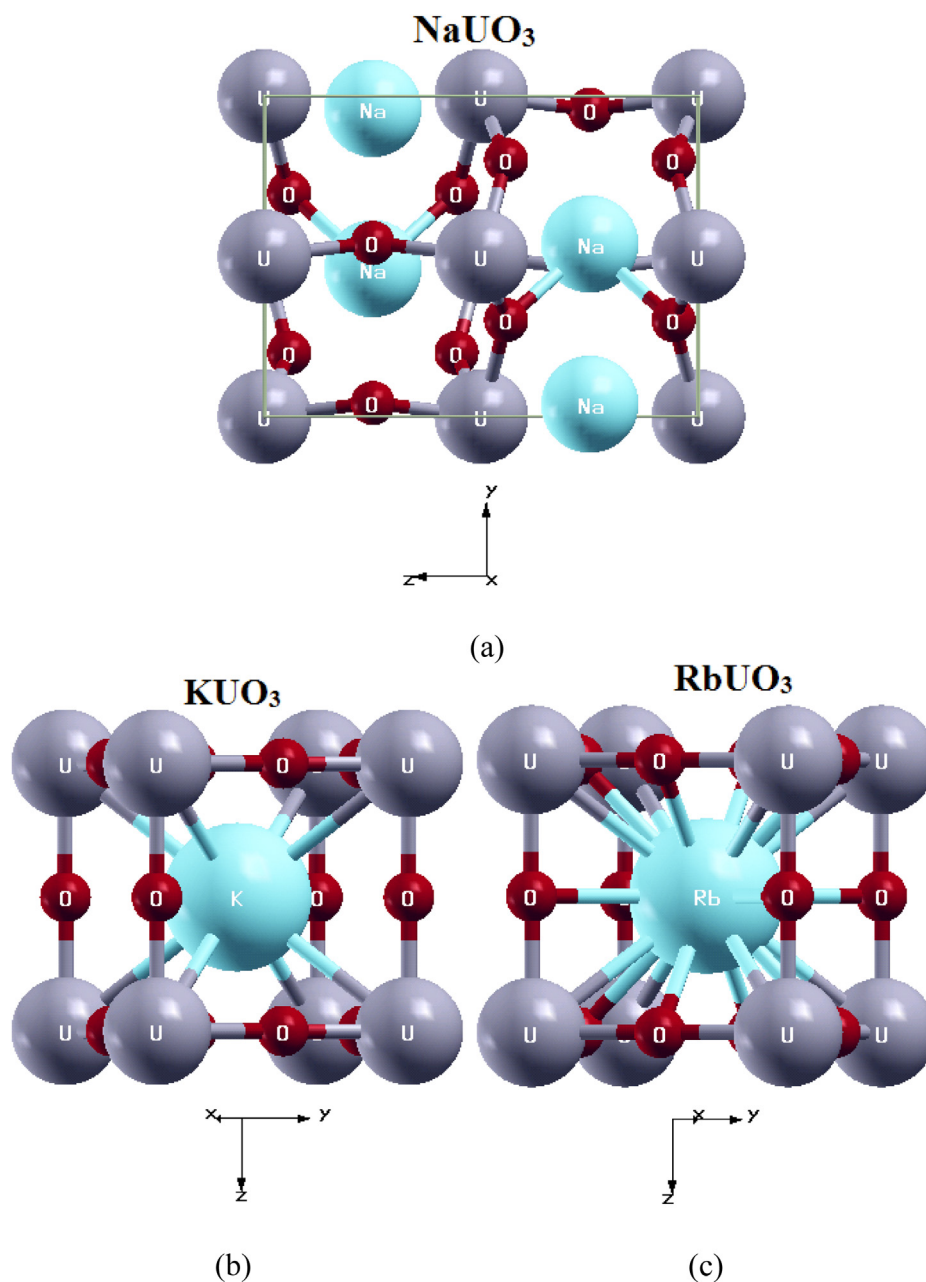


Fig. 1. Unit cell structure.

Table 1
Atomic positions.

Atoms	X	Y	Z
NaUO₃			
Cell parameters: $a = 5.7739$ (2) Å, $b = 5.9051$ (2) Å, $c = 8.2784$ (2) Å, S.G.: Pbnm (no. 62)			
Na	−0.0075(8)	0.0306(6)	1/4
U	1/2	0	0
O	0.0959(4)	0.4671(4)	1/4
O	0.6982(3)	0.2984(3)	0.0502(2)
KUO₃			
Cell parameters: $a = b = c = 4.2930$ (9) Å S.G.: Pm-3m (no. 221)			
K	1/2	1/2	1/2
U	0	0	0
O	1/2	0	0
RbUO₃			
Cell parameters: $a = b = c = 4.3222$ (9) Å S.G.: Pm-3m (no. 221)			
Rb	1/2	1/2	1/2
U	0	0	0
O	1/2	0	0

idea behind the GGA + U method comes from the Hubbard Hamiltonian. In the practical implementations, the on-site two-electron integrals, which would appear in Hartree–Fock like treatment, are expressed in terms of two parameters U and J, in which U corrects the strength of the on-site Coulomb interaction and J adjusts the strength of the exchange interaction. The choice of U is, however, not unambiguous and it is not trivial to determine the value, though there are attempts to extract it from standard first-principles calculations. Hence, U is often fitted to reproduce a certain set of experimental data, such as band gaps and structural properties. We used the approach formulated by Dudarev et al. to account for the strong on-site Coulomb repulsion [27].

Kohn–Sham wave functions were expanded in terms of spherical harmonic function in side the non-overlapping muffin-tin (MT) spheres and with Fourier series in the interstitial region. The ι -expansions of the wave functions were carried out up to $\iota_{\max} = 10$ inside the muffin-tin spheres of radius RMT. The Fourier expansion for the charge density was up to $G_{\max} = 12$. The wave functions in the interstitial regions were expanded in the plane waves for the cut off of $K_{\max} \times R_{\text{MT}} = 7$ in order to achieve the convergence for energy Eigen values. The muffin-tin radii of NaUO₃ compound are chosen as: $R_{\text{MT}}(\text{Na}) = 2.07$ a.u., $R_{\text{MT}}(\text{U}) = 2.01$ a.u. and $R_{\text{MT}}(\text{O}) = 1.78$ a.u., the value for muffin-tin radii for compound KUO₃ are chosen as $R_{\text{MT}}(\text{K}) = 2.5$ a.u., $R_{\text{MT}}(\text{U}) = 2.14$ a.u. and $R_{\text{MT}}(\text{O}) = 1.9$ a.u., and for RbUO₃ are chosen as $R_{\text{MT}}(\text{Rb}) = 2.5$ a.u., $R_{\text{MT}}(\text{U}) = 2.15$ a.u. and $R_{\text{MT}}(\text{O}) = 1.91$ a.u.

The optical calculations were computed in the momentum representation, which entails matrix elements of the momentum p between the valence and conduction bands. Thus, imaginary or the absorptive part of the dielectric function, the components $\epsilon_2^{ij}(\omega)$, was computed using the relation given in Ref. [28];

$$\epsilon_2^{ij}(\omega) = \frac{4\pi^2 e^2}{Vm^2\omega^2} \times \sum_{knm\sigma} \langle kn\sigma | p_i | kn'\sigma \rangle \langle kn'\sigma | p_j | kn\sigma \rangle \times f_{kn}(1 - f_{kn'})\sigma(E_{kn'} - E_{kn} - \hbar\omega) \quad (1)$$

where e is the electron charge and m is the and mass, ω is the frequency of the in coming electromagnetic radiation, V is the volume of the unit cell, $(p_x, p_y, p_z) = p$ is the momentum operator $|kn\sigma\rangle$ the crystal wave function, corresponding to eigen value E_{kn} with crystal momentum k and spin σ . Finally, f_{kn} is the Fermi distribution function ensuring that only transitions from occupied to

unoccupied states are counted, and $\sigma(E_{kn'} - E_{kn} - \omega)$ is the condition for total energy conservation. The real part $\epsilon_1(\omega)$ can be obtained from the imaginary part $\epsilon_2(\omega)$ using the Kramer's Kronig [29] dispersion relation.

Results and discussions

Electronic structure

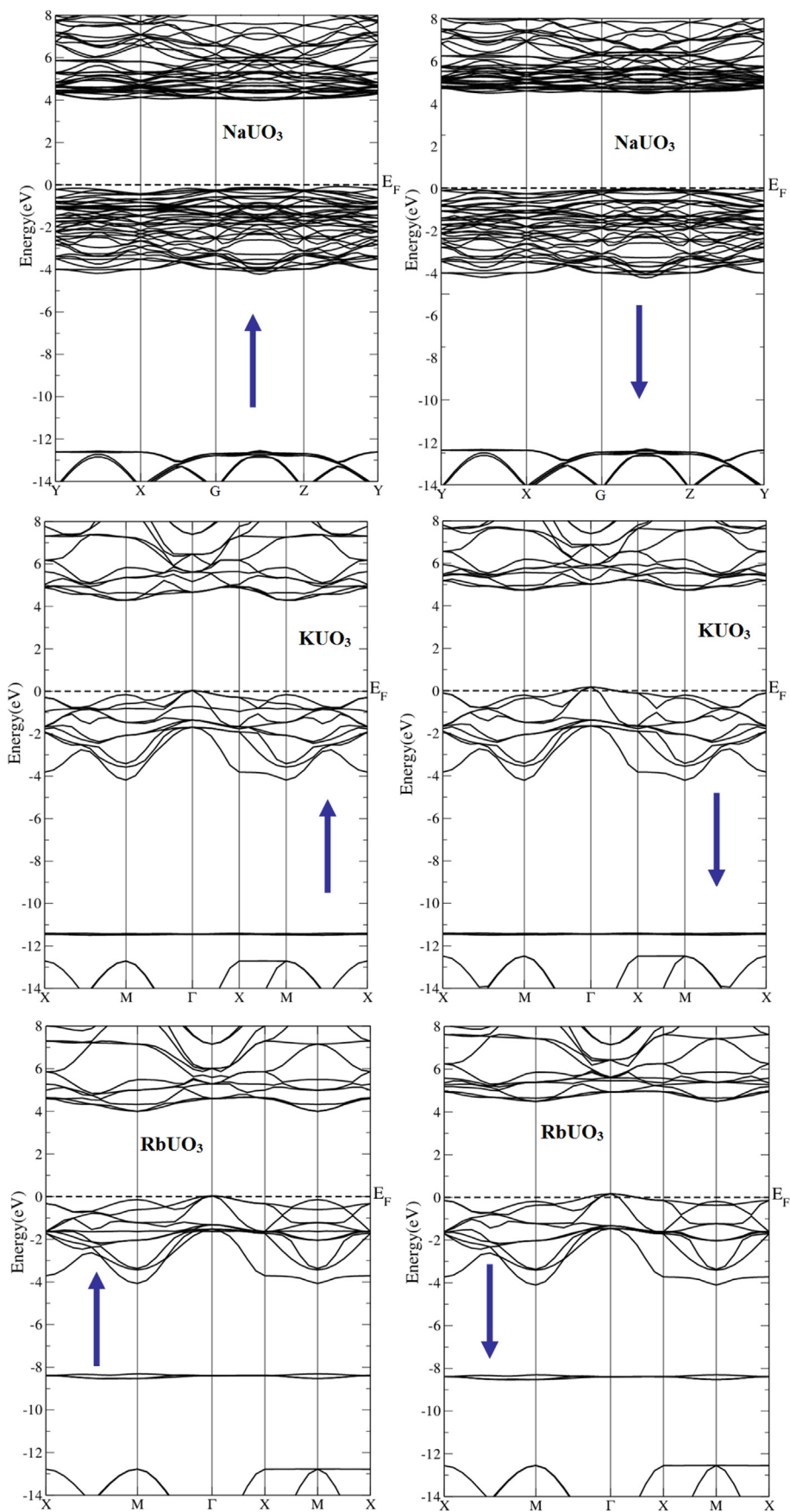
The present work using GGA + U treats the electronic structure of the MUO₃ (M = Na, K and Rb). In addition, we used the population analyses to elucidate the nature of the electronic band structure, densities of states and electronic charge density. The band structure and the total and partial densities of states in the spin polarized configuration within the GGA + U approach are shown in Fig. 2; this figure shows the three investigated compounds exhibit semi conducting behavior.

Electronic band structure plays a vital role in studying the materials and shows the value of energy gap E_g between the conduction band and valence band. We apply the type of method such as GGA + U in order to get better band gap value of the MUO₃ (M = Na, K and Rb) compound. Fig. 2 shows the band structure of MUO₃ (M = Na, K and Rb) compound. It can be seen that there is a direct/indirect energy gap of about 4.466, 4.652 and 4.326 eV for NaUO₃, KUO₃ and RbUO₃ respectively, using GGA + U approximation. The NaUO₃ compound has the direct band gap, the conduction and valence band maximum and minimum exist in between Γ and Z points, while the KUO₃ and RbUO₃ compounds have the indirect band gap, the conduction band minimum exists at M point while valence band maximum exists at Γ point.

Useful information can be gained from total density of states (TDOS) and partial density of states (PDOS) such as hybridization of states, bonding nature and contribution of orbitals to the electronic band structure. Fig. 3 illustrates TDOS and PDOS of Na/K/Rb, U and O atoms in MUO₃ (M = Na, K and Rb). PDOS express that valence band is mostly dominated by U-s/p/f and O-p states. While the conduction band is composed of U-f/d and Na/K/Rb-s/p orbitals. In the lower energy between -16 eV and -12 eV, U-s/p orbital and O-s orbitals mainly contribute, while from -4.0 eV to fermi level the O-p and U-s/f greatly contribute and also the small contribution of U-p/d and Na/K/Rb-s/p contribution has been observed. In conduction band the Na/K/Rb-s/p and U-d/f orbitals has greater contribution along with the small contribution of U-s orbitals has been observed for the three compounds. Strong hybridization means potential covalent bonding and less ionic character. Covalent bond is formed between U and O atom as can be seen from PDOS when U-p and O-d states hybridized between -0.2 .

Electron charge density

The electronic charge density signifies the scenery of the bond character. For predicting the chemical bonding and also the charge transfer in NaUO₃, KUO₃ and RbUO₃ compounds, the charge density behaviors in 2D are computed in the (110) plane for NaUO₃ and in (100) plane for KUO₃ and RbUO₃ as displayed in Fig. 4. To discuss the electronic charge density we have calculated the bond lengths in unit lattices of NaUO₃, KUO₃ and RbUO₃ compounds as given in Table 2. The result shows that the substitution of the Na by K and K by Rb leads to redistribution of electron charge density. As we replace Na by K the bond length between U and O atoms increases and again when we replace K by Rb again the increase in bond length occurs between U and O atoms. As an atom is interchanged by the other atom the VSCC (valence shell charge carrier) properties changes [29]. By investigating the influence of replacing of Na by K and K by Rb in NaUO₃, KUO₃ and RbUO₃ compounds, it has been

**Fig. 2.** Calculated band structures.

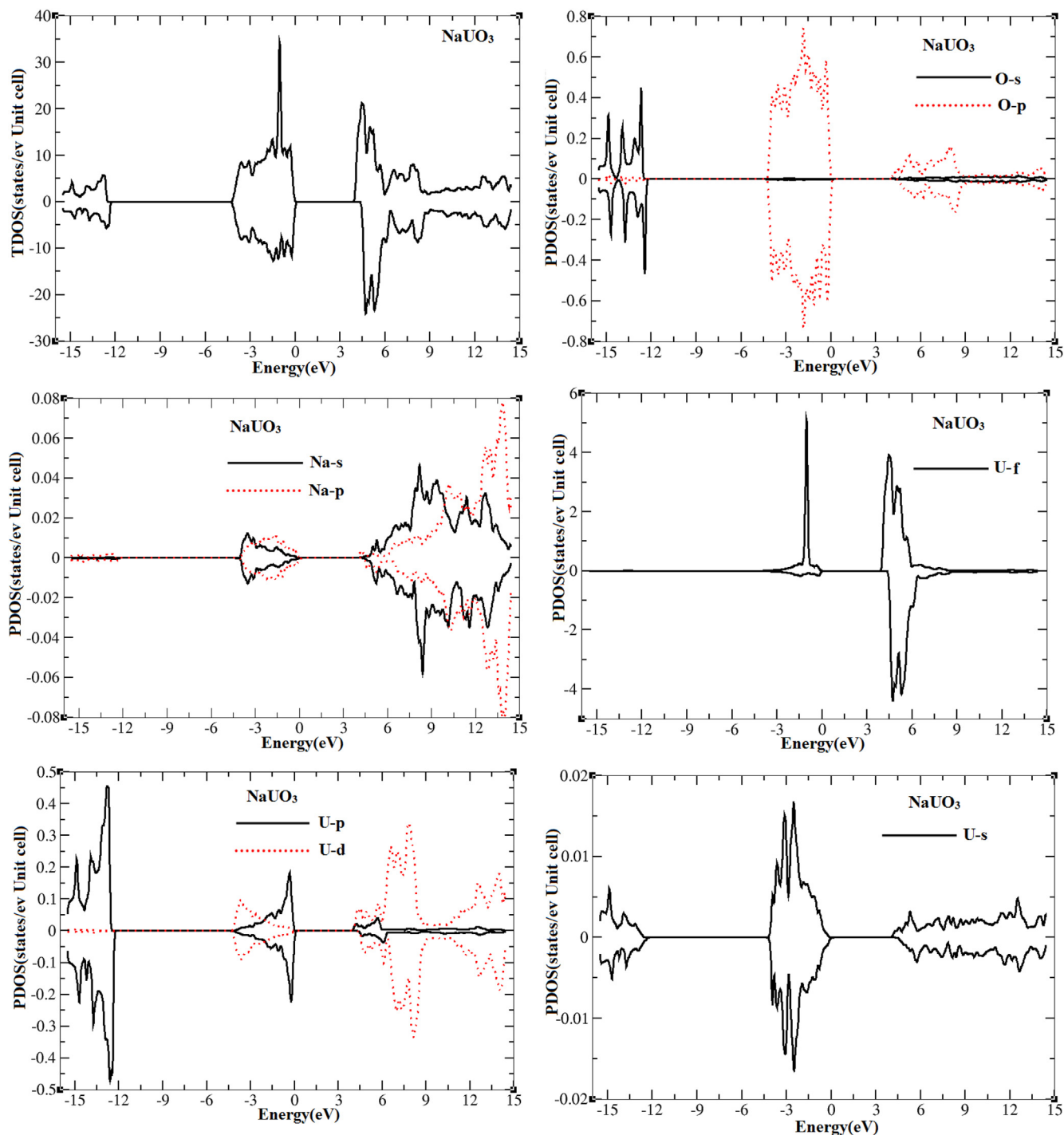


Fig. 3. Calculated total and partial densities of state.

found that oxygen atom make ionic bonding in the NaUO_3 which is absent in the other two compounds and also the bond length changes as it is clear from Table 2. From the calculated electron density it is clear that Na, K and Rb atoms forms an ionic bonding while the U and O atoms make strong covalent bonding.

Optical properties

In this section we will talk about the dielectric function (complex quantity) $\epsilon(\omega)$ of MUO_3 ($M = \text{Na, K and Rb}$) compounds. These

properties are resolute by the dielectric function $\epsilon(\omega)$ as specified by the following expression $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$. The dielectric function absorptive part, $\epsilon_2(\omega)$ contingents on the momentum matrix elements and the joint density of states. The optical properties can be illustrated through the transverse dielectric function $\epsilon(\omega)$. For $\epsilon(\omega)$, there exist two impacts i.e. the intraband and interband transitions. The contribution of first one is only vital for metals. While the former one, can be torn apart in to direct and indirect transitions. Here in this article we overlap the indirect interband transitions that implicate the scattering of phonons

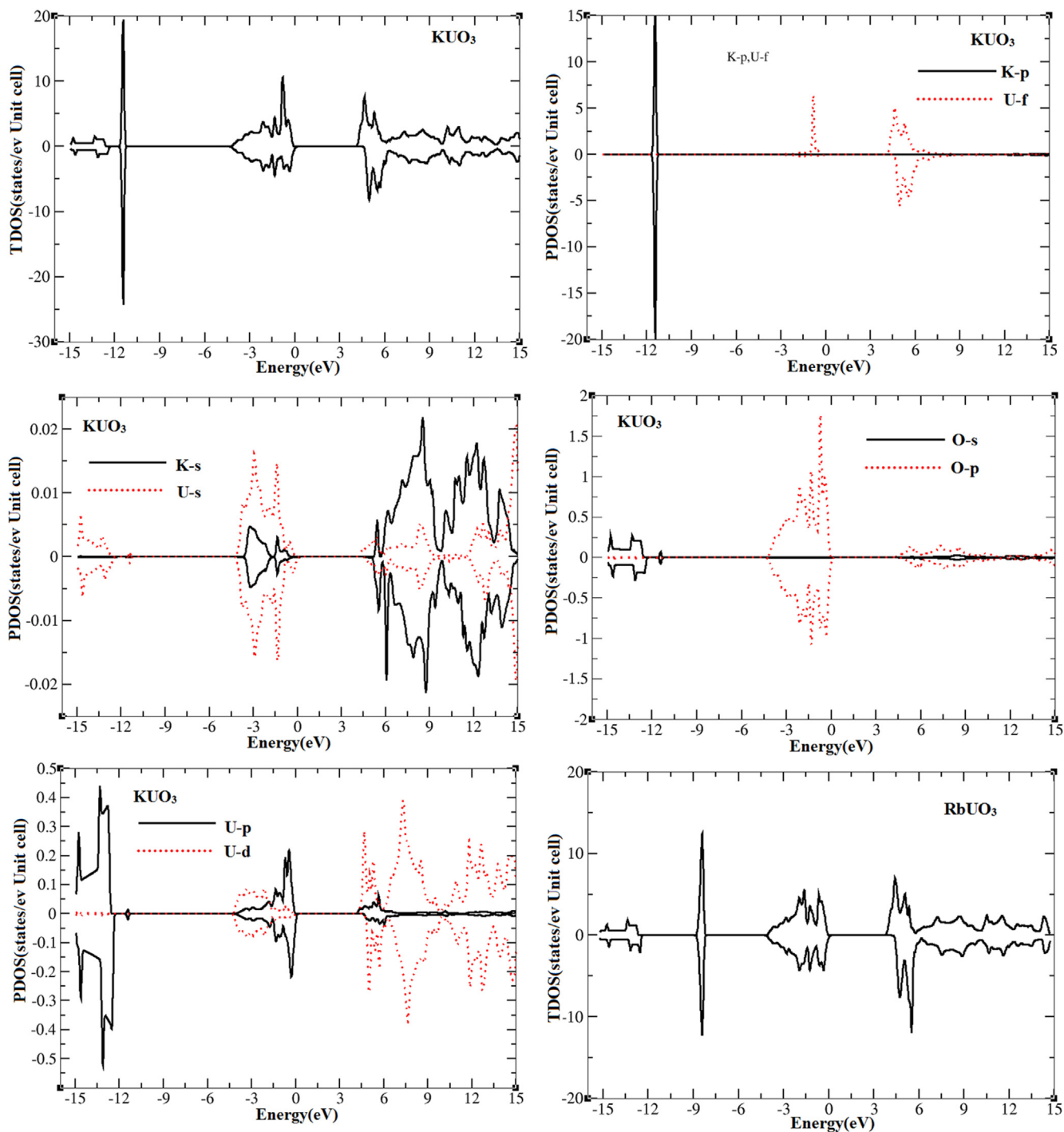


Fig. 3. (continued).

assuming a small contribution to the frequency dependent dielectric functions. For calculating the direct interband contribution to the absorptive part, so this is obligatory to summarize all conceivable transitions from valence band to the conduction band taking the suitable transition dipole matrix elements into description.

The NaUO_3 compound with orthorhombic symmetry has three nonzero components of the dielectric tensor. This compound communicate to an electric field perpendicular and parallel to the c -axis, which are filed as $\epsilon^{xx}(\omega)$, $\epsilon^{yy}(\omega)$ and $\epsilon^{zz}(\omega)$. We calculated the

average $\epsilon^{\text{average}}(\omega)$ value of NaUO_3 compound. While the KUO_3 and RbUO_3 compounds with cubic symmetry has $\epsilon^{xx}(\omega) = \epsilon^{yy}(\omega) = \epsilon^{zz}(\omega)$ nonzero components of the dielectric tensor. The premeditated spin up and down imaginary part for the inspected compounds have been exposed in Fig. 5a–c. The calculated reflectivity spectrum $\epsilon_2(\omega)$ of the cubic MUO_3 ($M = \text{K}; \text{Rb}$) compounds and $\epsilon_2^{\text{average}}(\omega)$ of NaUO_3 the orthorhombic compound.

It is apparent from the figure that there exists the anisotropy between the spin up and down spectra and its maximum peaks are found in between 5.0 eV and 9.0 eV for the three compounds. These

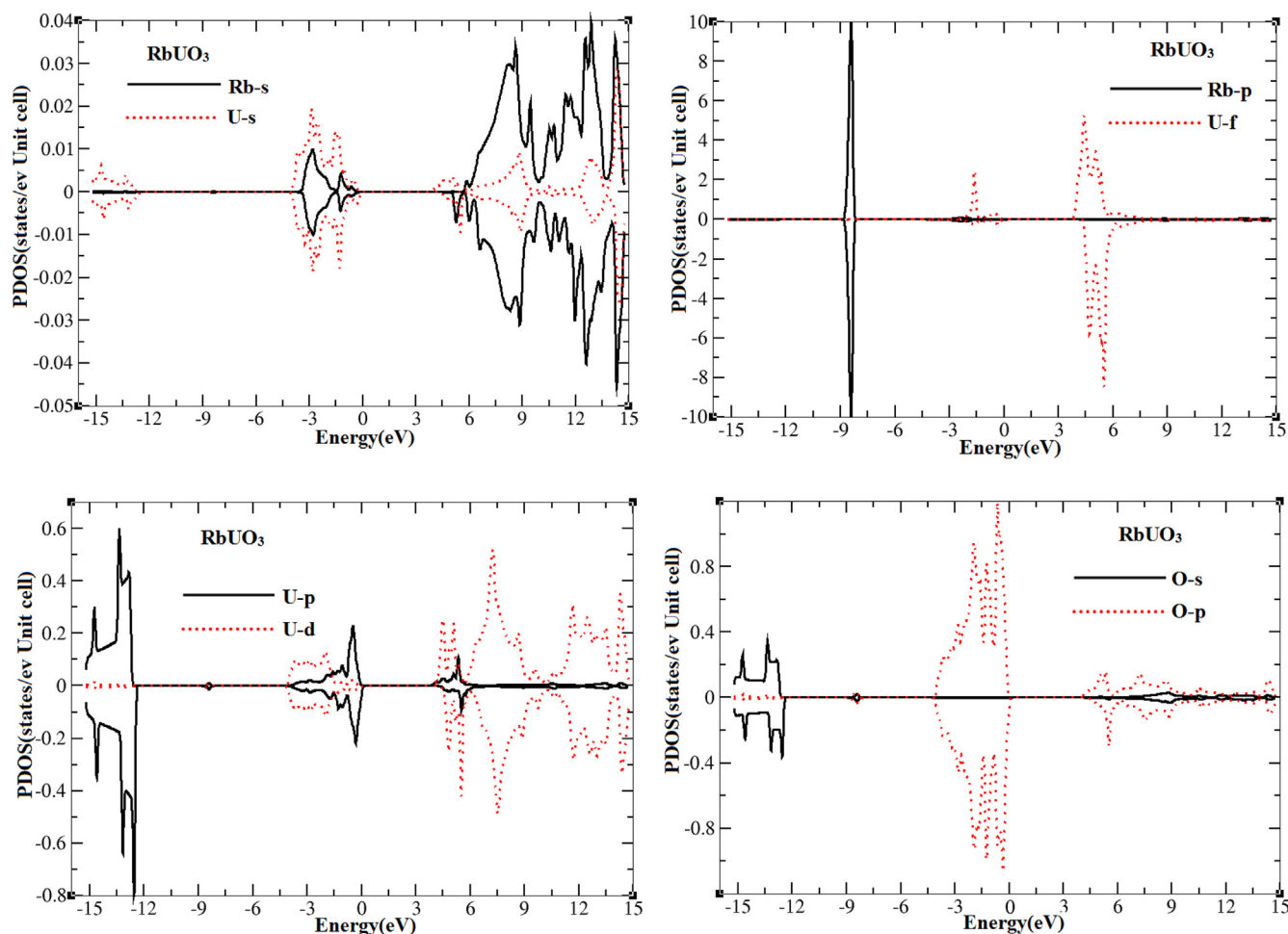


Fig. 3. (continued).

max out that emerged in Fig. 4 relate to an energy transition between a number of orbital analogous to definite energy because $\varepsilon_2(\omega)$ is related to the density of states (DOS) in contrast with Fig. 5a–c.

It can be acknowledged that the peaks are mostly owed to transitions from U-f valence bands to U-d conduction bands. Distant from the major peak, the subsequent peaks come up frequently from direct transitions between O-p U-f orbitals. At upper energy the spectrum crumbles incredibly rapidly with photon energy. The consequences for the scattered part of the dielectric function, $\varepsilon_1(\omega)$ is prearranged in Fig. 6a–c. The calculated real part spectrum $\varepsilon_1(\omega)$ of the cubic MUO₃ (M = K; Rb) compounds and $\varepsilon_1^{\text{average}}(\omega)$ of NaUO₃ the orthorhombic compound.

At higher frequencies the zero of $\varepsilon_1(\omega)$, which relates to the position of the screened plasma frequency is positioned at 4.7 eV and in addition at elevated energies. The static dielectric constant $\varepsilon_1(\omega)$ is specified by the small energy edge of $\varepsilon_1(\omega)$. It is obligatory to highlight that we do not comprise phonon assistance to the dielectric screening, and $\varepsilon_1(\omega)$ recounts to the static optical dielectric constant. There exists anisotropy between the up and down states of the three compounds. The attained optical dielectric constants following the GGA + U formalism beside the crystal axes resolve into the three compounds are listed in Table 3.

By means of the estimated dispersions of imaginary and real components of the frequency dependent dielectric function one can evaluate further optical properties for instance refractive index

$n(\omega)$, absorption coefficient $I(\omega)$, reflectivity $R(\omega)$ and energy loss function $L(\omega)$ for the spin up and down for the three compounds. These are shown in Figs. 7–10. Fig. 7a–c shows the calculated absorption coefficient spectrum $I(\omega)$ of the cubic MUO₃ (M = K; Rb) compounds and $I^{\text{average}}(\omega)$ of NaUO₃ the orthorhombic compound. The absorption bands in the explored collection is due to the inter ion transitions shown in Fig. 7a–c. We monitor that the deliberated compounds have other powerful optical absorptions at higher energies. The enormity of the absorption coefficients of these crests, i.e. peak consents an optical transition due to excitons. In the vicinity of the absorption peaks, the absorption coefficients are bulky and demonstrate an allowed optical transition, almost certainly to an excitation level. The intended outcome here present that all the absorption spectra of the compound exhibit a number of absorption peaks in the fundamental absorption region. Fig. 8a–c shows the calculated energy loss spectrum $L(\omega)$ of the cubic MUO₃ (M = K; Rb) compounds and $L^{\text{average}}(\omega)$ of NaUO₃ the orthorhombic compound. The electron energy loss function narrates the interaction by which the energy is lost by a fast going electron traveling in the material. The interactions may encompass phonon excitation, interband and intraband transitions, plasmon excitations and inner shell ionizations. The energy loss is generally large at the plasma frequencies. There exists the anisotropy between the spin up and down spectra of the three compounds. The peaks of the energy loss exist for the three compounds at higher energies, i.e. from 10.0 eV to 14.0 eV. These peaks correspond to the different energy ranges,

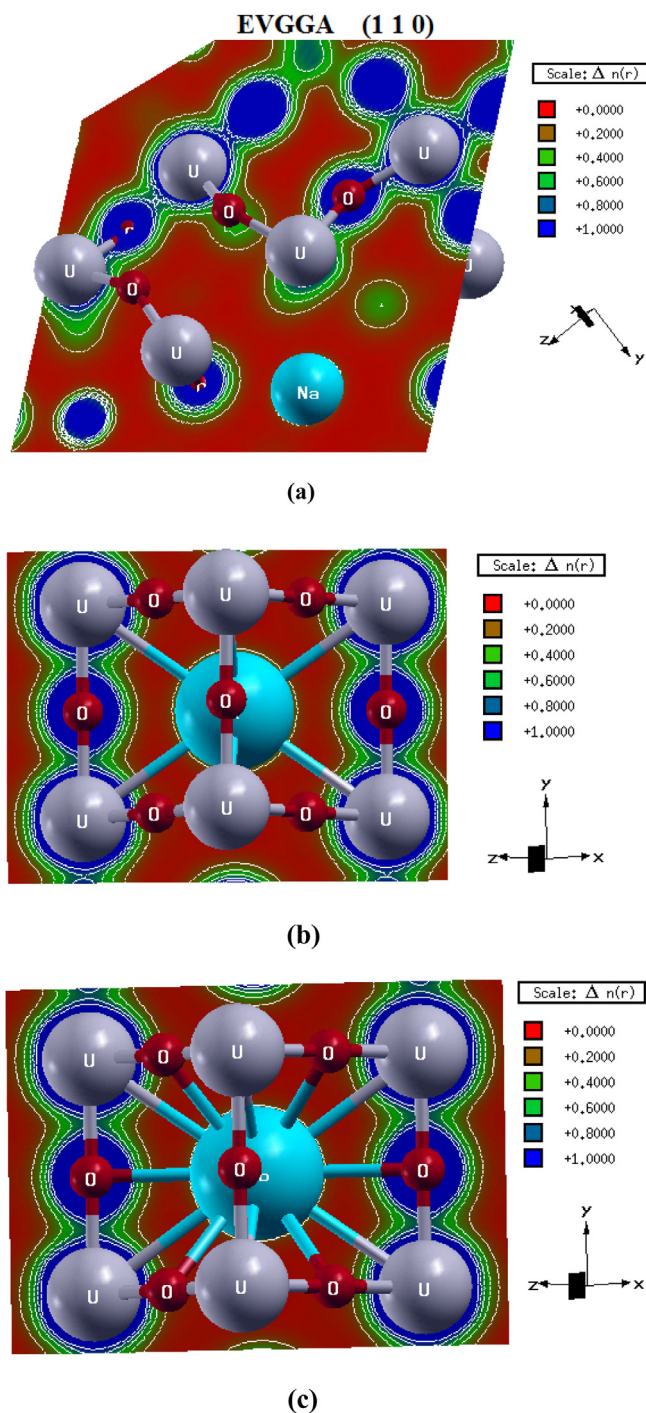


Fig. 4. Calculated charge density.

Table 2
Bond length.

NaUO ₃		KUO ₃		RbUO ₃	
U–O1	2.122	U–O	2.147	U–O	2.161
Na–O1	2.576	K–O	3.076	Rb–O	3.056
Na–O2	2.777	U–K	3.178	Rb–U	3.743
U–Na	3.381				

corresponding to electrical devices excitations of different orbitals. The greatest peaks in the energy loss function are affiliated with the reality of plasma oscillations. Fig. 9a–c shows the calculated reflectivity spectrum $R(\omega)$ of the cubic MUO₃ (M = K; Rb)

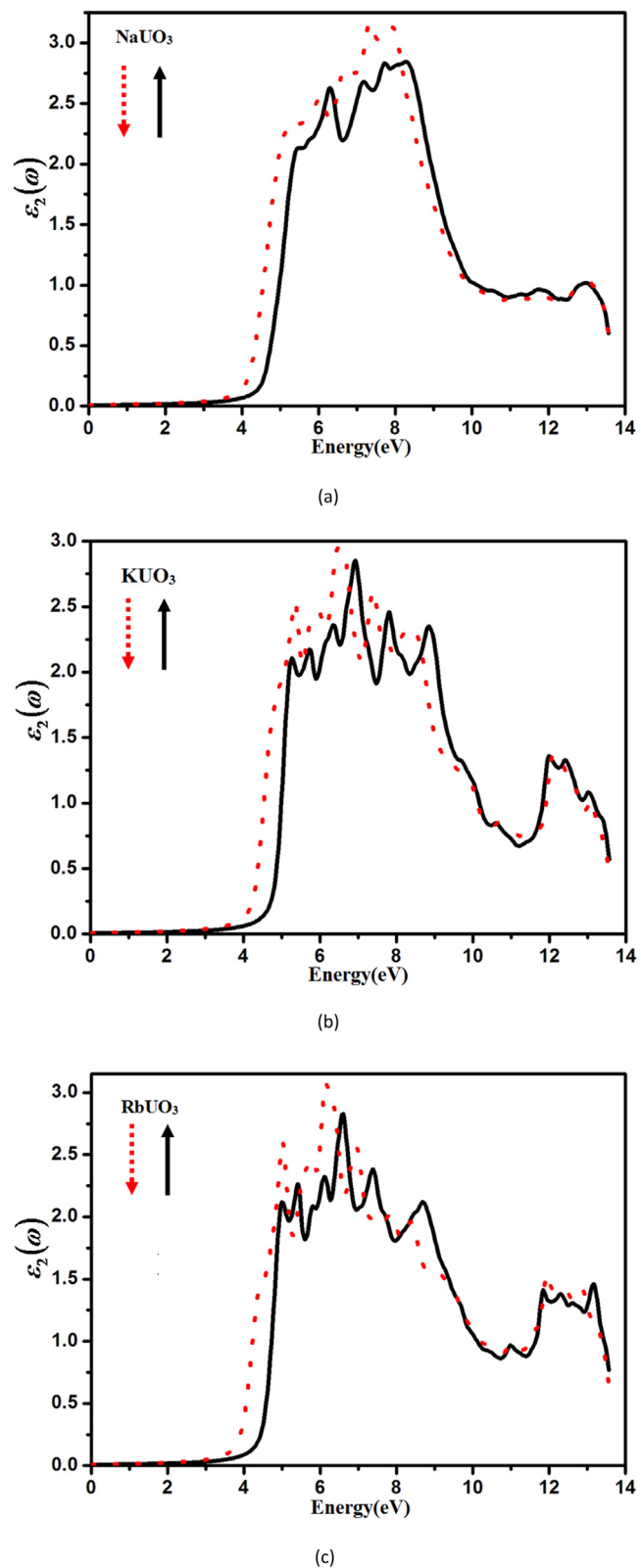


Fig. 5. Calculated imaginary part of dielectric tensor function.

Table 3
 $\epsilon_1(0)$ optical dielectric constant values.

	NaUO ₃	KUO ₃	RbUO ₃
Up	2.25	2.18	2.15
Dn	2.4	2.30	2.30

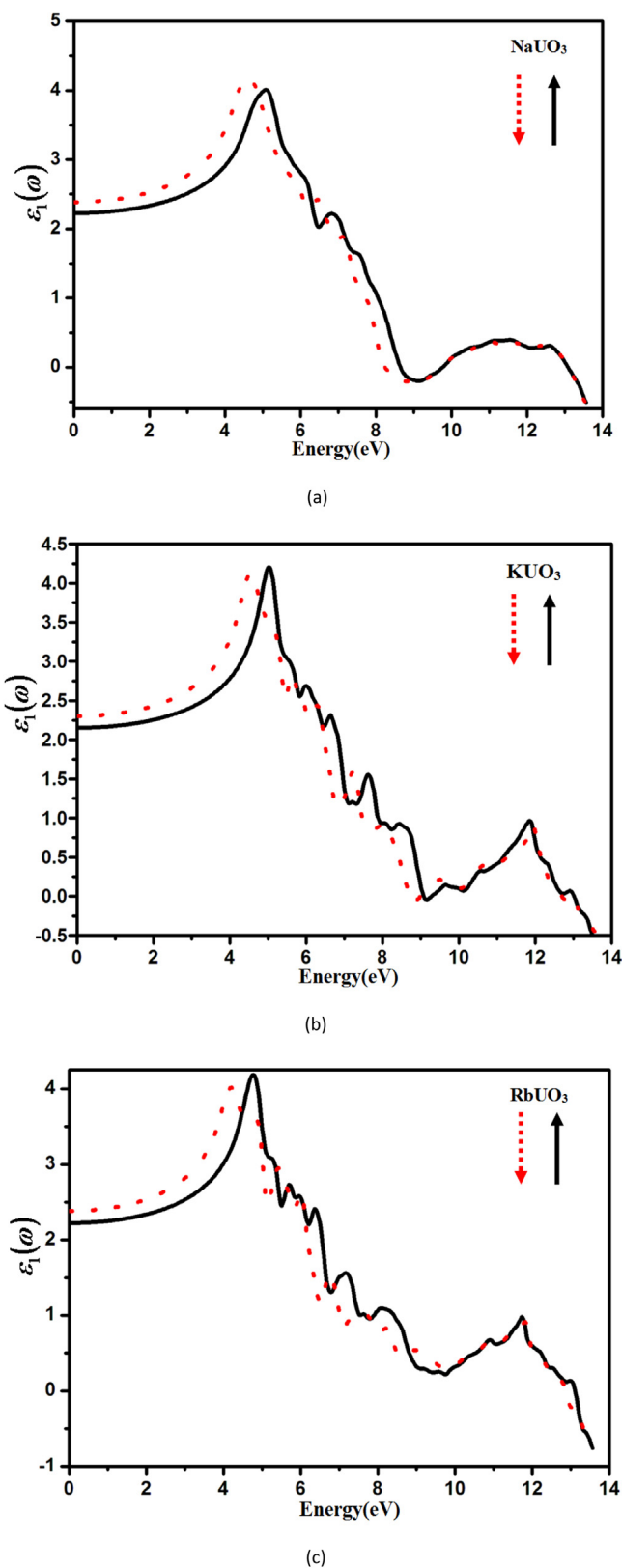


Fig. 6. Calculated real part of dielectric tensor function.

compounds and $R^{\text{average}}(\omega)$ of NaUO₃ the orthorhombic compound. These compounds display low reflectivity at initial energies, i.e. from 0.0 eV to 4.0 eV, which quickly increases with increasing the energies up to 9.0 eV, and again decreases with increasing the

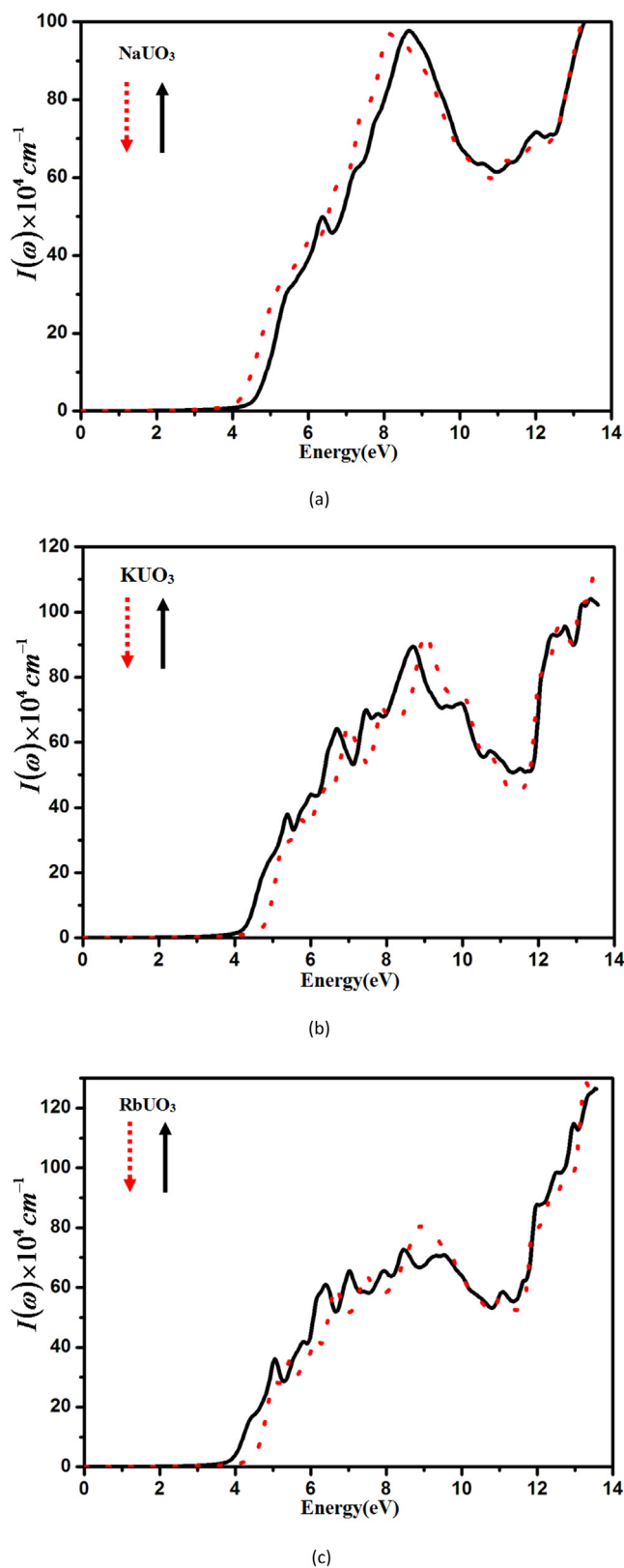
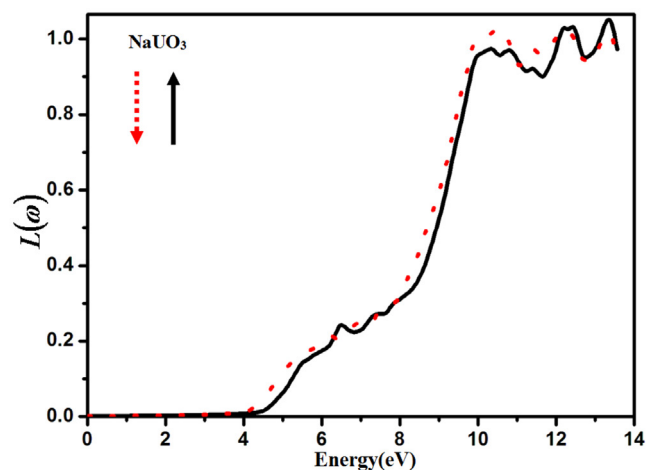
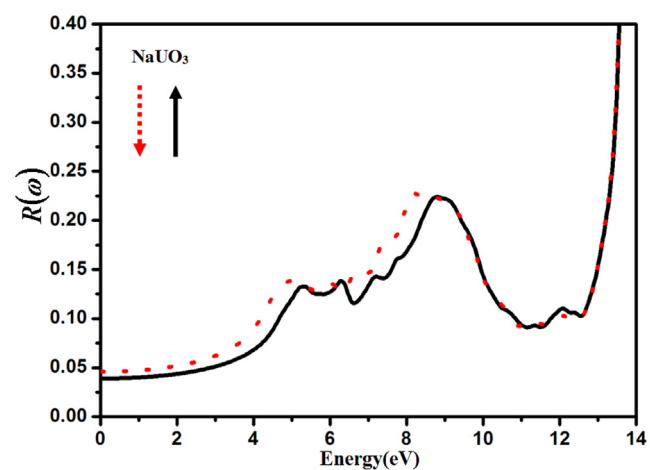


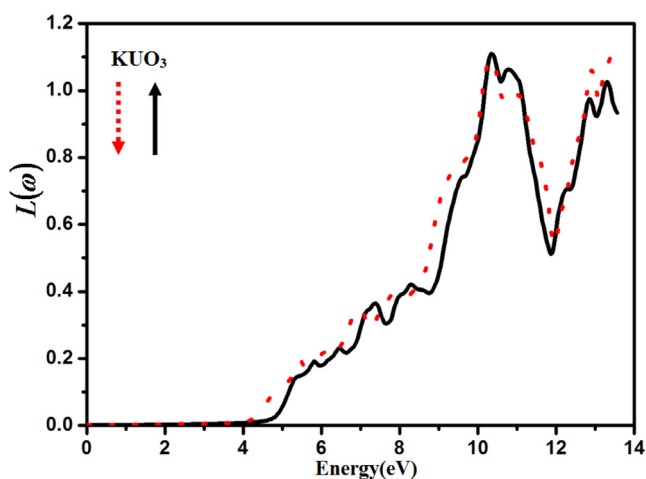
Fig. 7. Calculated absorption coefficient spectrum.



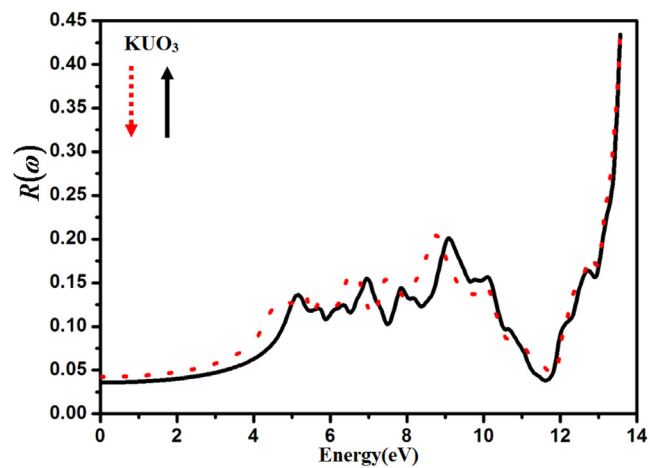
(a)



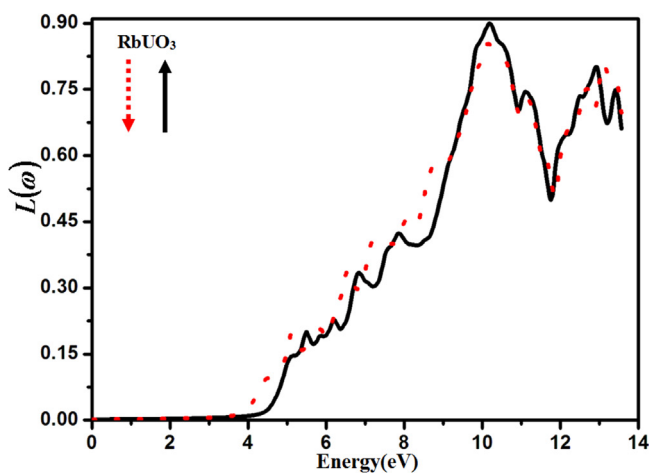
(a)



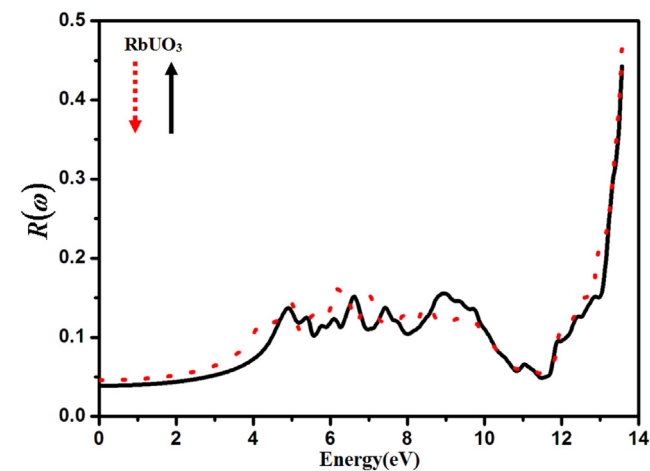
(b)



(b)



(c)



(c)

Fig. 8. Calculated energy loss spectrum.

Fig. 9. Calculated reflectivity spectrum.

energies up to 12.5 eV. The spectra again increases increasing the energy and reaches to the maximum at 13.5 eV. Fig. 10a–c shows the calculated refractive index spectrum $n(\omega)$ of the cubic MUO₃ (M = K; Rb) compounds and $n^{\text{average}}(\omega)$ of NaUO₃ the orthorhombic compound. Fig. 10a–c displays the variation of refractive index as a

function of incident photon energy for the spin up and down for the three compounds. We note that at 3.0–7.0 eV range the material shows high refractive index and then proceeds to smaller standards at the high powers for the three compounds. There also exists the anisotropy between the spin up and down states.

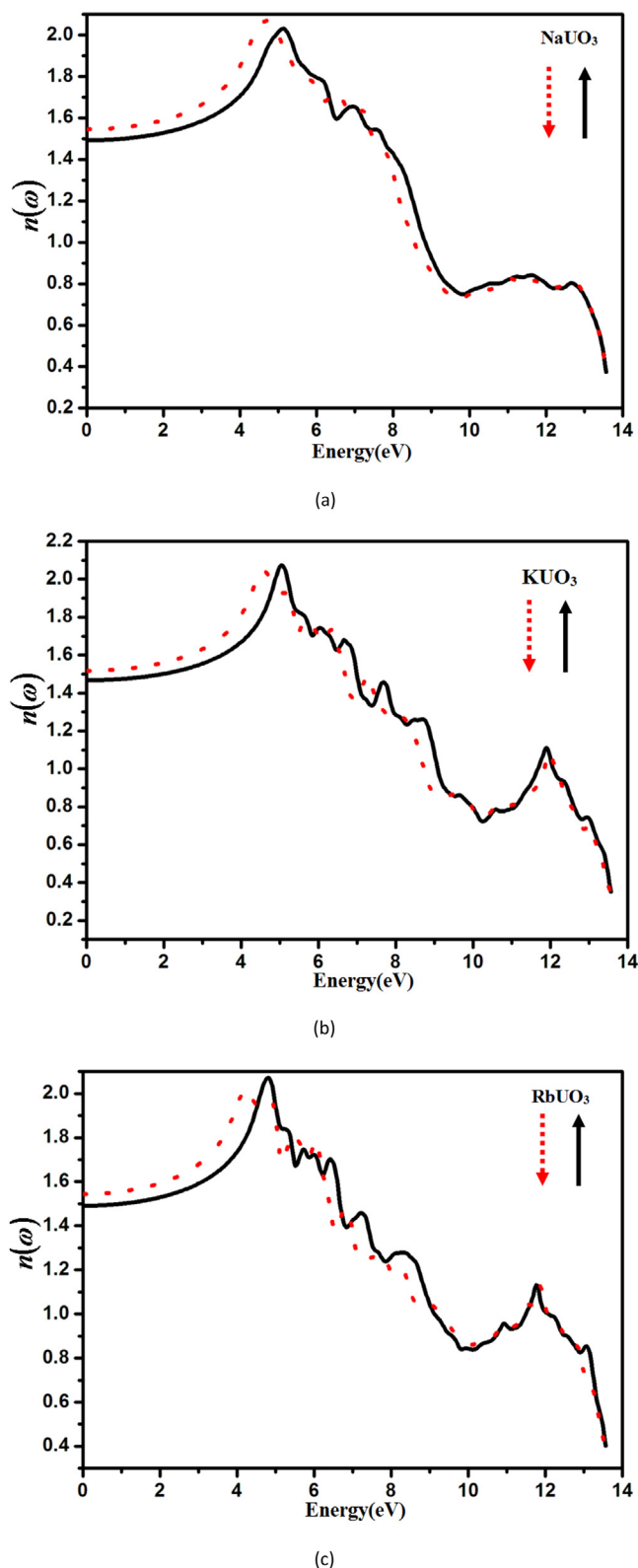


Fig. 10. Calculated refractive index.

Conclusion

We scrutinize the electronic structure and electronic charge density of MUO_3 ($M = Na; K; Rb$) compound within a framework of DFT based on full potential calculations. We have employed the

GGA + U to treat the exchange correlation potential by solving Kohn–Sham equations. It is well known that density functional theory (DFT) underestimates band gaps of materials which have highly localized valence electrons. On the other hand, the predictions of electronic properties of materials, which do not have localized band near the band gap, by DFT are not accurate enough as well. The effect of electronic correlation on properties of MUO_3 ($M = Na; K; Rb$) compound is theoretically studied in this paper. The calculations show that the investigated compounds are semiconductor with direct/indirect energy gap of about 4.466, 4.652 and 4.326 eV for $NaUO_3$, KUO_3 and $RbUO_3$, respectively. The density of states express that valence band is mostly dominated by U-s/p/f and O-p states. While the conduction band is composed of U-f/d and Na/K/Rb-s/p orbitals. Covalent bond is formed between U and O atom as can be seen from PDOS when U-p and O-d states hybridized between -0.2 . The electronic charge density study shows that the substitution of the Na by K and K by Rb leads to redistribution of electron charge density. As we replace Na by K the bond length between U and O atoms increases and again when we replace K by Rb again the increase in bond length occurs between U and O atoms. The imaginary and real parts of the dielectric function were also discussed in particulars. By means of the estimated dispersions of imaginary and real components of the frequency dependent dielectric function one can evaluate further optical properties for instance refractive index $n(\omega)$, absorption coefficient $I(\omega)$, reflectivity $R(\omega)$ and energy loss function $L(\omega)$ for the spin up and down for the three the three compounds.

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References

- [1] S. Von Kemmler-Sack, E. Stumpp, W. Rudorff, H. Erfurth, *Magnetismus des U(V)-ions in ternären oxiden*, Z. Anorg. Allg. Chem. 354 (1967) 287–300.
- [2] S. Bartram, R. Fryxell, J. Inorg. Nucl. Chem. 32 (1970) 3701–3706.
- [3] A. Van Egmond, E. Cordfunke, J. Inorg. Nucl. Chem. 38 (1976) 2245–2247.
- [4] W. Lyon, D. Osborne, H. Flotow, H. Hoekstra, J. Chem. Thermodyn. 9 (1977) 201–210.
- [5] C. Miyake, K. Fuji, S. Imoto, Chem. Phys. Lett. 46 (2) (1977) 349–351.
- [6] C. Miyake, K. Fuji, S. Imoto, Chem. Phys. Lett. 61 (1) (1979) 124–126.
- [7] B. Kanellakopoulos, E. Henrich, C. Keller, F. Baumgartner, E. König, V. Desai, Chem. Phys. 53 (1980) 197–213.
- [8] C. Miyake, H. Takeuchi, K. Fuji, S. Imoto, Phys. Stat. Sol. 83 (1984) 567–572.
- [9] C. Miyake, M. Kanamura, H. Anada, S. Imoto, S. Kawano, J. Nucl. Sci. Technol. 22 (8) (1985) 653–657.
- [10] A. Chippindale, P. Dickens, W. Harrison, J. Solid State Chem. 78 (1989) 256–261.
- [11] P. Dickens, A. Powell, J. Mater. Chem. 1 (1991) 137–138.
- [12] Y. Hinatsu, T. Fujino, N. Edelstein, J. Solid State Chem. 99 (1992) 182–188.
- [13] Y. Hinatsu, J. Solid State Chem. 110 (1994) 118–123.
- [14] Y. Hinatsu, J. Alloys Compd. 203 (1994) 251–257.
- [15] Y. Hinatsu, Y. Shimojo, Y. Morri, J. Alloys Compd. 270 (1998) 127–131.
- [16] L.R. Morss, N.M. Edelstein, J. Fuger, J.J. Katz (Eds.), *The Chemistry of the Actinide and Transactinide Elements*, Springer, Berlin, 2006, p. 3015.
- [17] S. Van den Berghe, M. Verwerft, J.-P. Laval, B. Gaudreau, P.G. Allen, A. Van Wyngarden, J. Solid State Chem. 166 (2002) 320–329.
- [18] G.C. Allen, J.A. Crofts, M.T. Curtis, P.M. Tucker, J. Chem. Soc. Dalton Trans. (1974) 1296–1301.
- [19] M.A. Denecke, *Coord. Chem. Rev.* 250 (2006) 730–754.
- [20] A. Bianconi, in: R. Prins, D.C. Koningsberger (Eds.), *X-ray Absorption: Principles, Applications and Techniques of EXAFS, SEXAFS and XANES*, Wiley, New York, 1988, p. 573.
- [21] S. Van den Berghe, A. Leenaers, C. Ritter, J. Solid State Chem. 177 (2004) 2231–2236.
- [22] O.K. Andersen, *Phys. Rev. B* 12 (1975) 3060–3083. D.J. Singh, *Plane Waves, Pseudopotentials and the LAPW Method*, Kluwer Academic, Dordrecht, 1994.
- [23] K.M. Wong, S.M. Alay-e-Abbas, A. Shaikat, Y. Fang, Y. Lei, J. Appl. Phys. 113 (2013) 014304.

- [24] K.M. Wong, S.M. Alay-e-Abbas, Y. Fang, A. Shaukat, Y. Lei, *J. Appl. Phys.* 114 (2013) 034901.
- [25] P. Blaha, K. Schwarz, G.K.H. Madsen, D. Kvasnicka, J. Luitz, *An Augmented Plane Waves+Local Orbital Program for Calculating Crystal Properties*, Institut Für Physikalische und Theoretische Chemie, Wien, Austria, 2001.
- [26] J.P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* 77 (1996) 3865.
- [27] S.L. Dudarev, G.A. Botton, S.Y. Savrasov, C.J. Humphreys, A.P. Sutton, *Phys. Rev. B* 57 (1998) 1505.
- [28] A. Sikander Azam, H. Reshak, *Int. J. Electrochem. Sci.* 8 (2013) 10359–10375.
- [29] F. Wooten, *Optical Properties of Solids*, Academic Press, New York, 1972.