

Electronic and optical properties of NH_4NO_3 and NaNO_3 : an ab initio study

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Received: 19 September 2015 / Accepted: 24 November 2015

Abstract: Structural, electronic and optical properties of inorganic aerosols, including ammonium nitrate NH_4NO_3 and sodium nitrate NaNO_3 have been investigated using the pseudo-potential plane wave scheme in the frame of generalized gradient approximation. The geometrical parameters of the unit cell have been fully optimized and are in good agreement with the experimental data. The electronic structures show that NH_4NO_3 and NaNO_3 have a direct gap of 3.21 eV and indirect band gap of 2.92 eV, respectively. The optical constants, including the dielectric function, refractive index, extinction coefficient, reflectivity and energy-loss spectra have been calculated and discussed. NH_4NO_3 and NaNO_3 absorb in the ranges [75–350] and [60–380] nm respectively.

Keywords: Ab initio; Inorganic aerosols; Ammonium nitrate; Sodium nitrate; Electronic structure; Optical properties

PACS Nos.: 71.20.-b; 71.20.Ps; 78.20.Ci

1. Introduction

Aerosols particles are ubiquitous in the troposphere. They influence climate through scattering, transmission and absorption of radiation as well as by acting as nuclei for cloud formation [1]. Tropospheric aerosols are essentially composed of inorganic salts [2]. Because of their potential environmental impacts, the properties of ammonium nitrate (NH_4NO_3) and sodium nitrate (NaNO_3) particles are widely investigated.

The thermodynamic properties of NH_4NO_3 have been studied at ambient temperature [3]. Many efforts have been made to study this aerosol under ambient tropospheric and stratospheric conditions [4, 5]. For laboratory studies, infrared [6, 7] spectroscopy has been used to inspect vibrational properties of NH_4NO_3 . Also, hygroscopicity and evaporation of NH_4NO_3 have been studied [6–8]. Excimer laser fragmentation-fluorescence spectroscopies (ELFFS) have been used to make quantitative measurements of

ammonium nitrate particles [9]. Theoretically, first principles calculations using ab initio theory have been employed in a number of investigations [10, 11] to study proton transfer and electronic properties of ammonium nitrate.

Infrared (IR) and neutron diffusion studies [12–15] have been used to investigate vibrational properties of sodium nitrate. Additionally, hygroscopicity and evaporation of sodium nitrate have been studied [16, 17]. Absorption of non-polarized light by NaNO_3 crystal has been used to study the optical properties [18]. On the theoretical point of view, first principles calculations using ab initio quantum mechanical method based on periodic Hartree–Fock (PHF) theory have been performed [19, 20] to investigate the electronic properties of the crystalline material for bulk, clean and defected surfaces.

The structure and vibrational spectra of ammonium nitrate and sodium nitrate crystals have been investigated at the periodic ab initio quantum mechanical level using different approximations in the density functional theory [21].

In this work, we have presented a series of first-principles density functional theory calculations on the electronic

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structures for ammonium nitrate and sodium nitrate crystals. Furthermore, we have studied the optical properties including, the dielectric function, extinction coefficient, refractive index, reflectivity and energy-loss spectra. We have compared our results with the available experimental data as well as previous theoretical published values.

2. Methods

We have performed calculations using the commercial version of the software package CASTEP [22]. This program evaluates the total energy of periodically repeating geometries based on density-functional theory [23, 24] and the pseudo-potential approximation. The valence electrons are represented explicitly in the calculations, while, the valence-core interaction is described by nonlocal pseudo-potential. We have used the norm-conserving pseudo-potential of the form suggested by Kleinman and Bylander [25], with an energy cut-off of 1200 eV. The exchange–correlation potential is treated within Perdew–Wang (PW91) gradient corrected exchange and correlation functional [26–29]. The Brillouin zone is sampled with the Monkhorst–Pack scheme with mesh parameters $2 \times 3 \times 3$ [30]. The structural parameters of ammonium nitrate and sodium nitrate are determined using the Broyden Fletcher Goldfarb Shanno (BFGS) minimization technique [31] with the following thresholds for converged structure, energy change per atom less than 10^{-7} eV, residual force less than 0.002 eV/Å, stress below 0.01 GPa, and the displacement of atoms during the geometry optimization less than 0.0001 Å.

The optical properties of matter can be described by means of the dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$. The imaginary part is calculated from the momentum matrix elements between the occupied and unoccupied wave functions within the selection rules. The real part of dielectric function follows the Kramer-Kronig relationship. There are two contributions to $\varepsilon(\omega)$, namely, intraband and interband transitions. The contribution from intraband is important only for metals. The interband transitions can further be split into direct and indirect transitions. All other optical constants on the energy dependence, such as the refractive index $n(\omega)$, extinction coefficient $k(\omega)$, reflectivity $R(\omega)$ and energy-loss spectrum $L(\omega)$, are derived from $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$.

3. Results and discussion

3.1. Geometries

Ammonium nitrate IV is stable in the temperature range of 255–305 K. The structure of ammonium nitrate IV has been characterized by X-ray and neutron diffraction studies

[32–34]. The structure is orthorhombic, with space group $Pmmn$ with two NH_4NO_3 formula units per unit cell as shown in Fig. 1.

At room-temperature phase, sodium nitrate NaNO_3 belongs to the rhombohedral space group ($R\bar{3}c$) and has two NaNO_3 formula units in the unit cell as exposed in Fig. 2; the two NO_3^- ions are oriented in planes perpendicular to the optic axis [35].

The optimized structural parameters for ammonium nitrate IV are shown in Table 1 and compared with previous experimental results [33]. Our structural properties are consistent with the earlier experimental and theoretical results [10, 21, 33]. Our calculations confirm that N-O1 bond length is longer than N-O2 as shown previously [10, 21, 33]. It is worth noting that the positions of hydrogen atoms are not known to great accuracy in X-ray diffraction structures.

For sodium nitrate, the bond lengths and bond angles of the optimized structure are listed in Table 2. Our calculations corroborate with the theoretical published values [21]. The bond lengths are underestimated and the bond angles are overestimated by about a few percent compared with the calculated ones [21].

3.2. Electronic properties

The energy band structures for ammonium nitrate and sodium nitrate at equilibrium geometry along the high-symmetry directions in the Brillouin zone (BZ) are illustrated in Figs. 3 and 4 respectively. The energy of the highest occupied crystalline orbital has been set to zero. The bands are almost flat across the Brillouin zone, which is consistent with the ionic character of these crystals as shown in previous studies [10, 19, 20]. In our study, the Mulliken population analysis confirms essentially this ionic

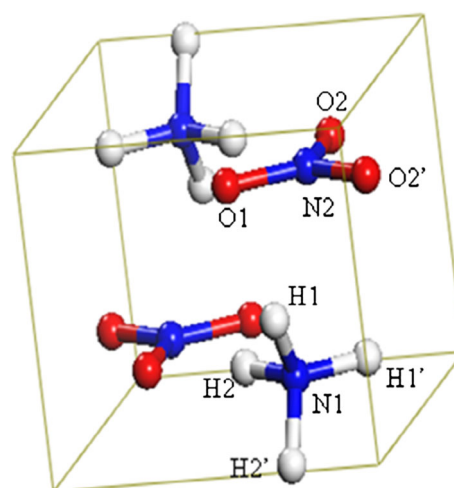


Fig. 1 Crystal structure of unit cell of ammonium nitrate IV

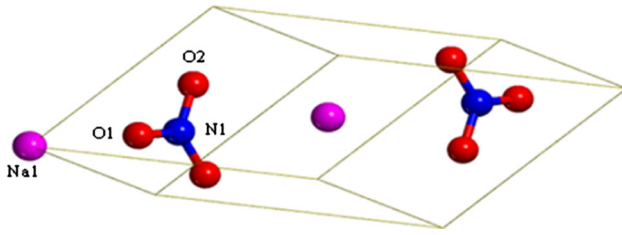


Fig. 2 Crystal structure of unit cell of sodium nitrate

Table 1 Calculated, experimental and theoretical equilibrium structural parameters for ammonium nitrate IV

Parameters	This work	Expt. value ^a
Bond lengths (Å)		
N2–O1	1.209	1.274
N2–O2	1.150	1.254
N1–H1	1.039	1.069
N1–H2	1.032	1.072
Bond angles (deg)		
O1–N2–O2	118.7	120.0
O2–N2–O2'	122.7	120.0
H1–N1–H1'	112.0	115.7
H1–N1–H2	109.1	107.9
H2–N1–H2'	108.3	109.4
Hydrogen bonds parameters (Å, deg)		
H1...O1	1.936	2.050
N1–H1...O1	158.0	154.4
H2...O1	2.031	2.161
N1–H2...O1	170.2	172.6

^a Ref. [33]

picture. As in the case of NH_4NO_3 , Mulliken charges indicate net charge of $-0.83|e|$ on the nitrate group and $+0.83|e|$ on the ammonium.

Ammonium nitrate has a direct band gap of 3.21 eV determined at Z point. This value is in a good agreement with that of 3.18 eV reported earlier [10]. For sodium nitrate, the top of the valence band (VB) exhibits the energy maximum at the F point, while the conduction band (CB) has its energy minimum at Γ point in the BZ. Therefore, the band gap in NaNO_3 crystal is indirect and its calculated value was 2.92 eV. It is well known that the GGA calculation underestimates the fundamental gap of semiconductors and insulators; so ammonium nitrate and sodium nitrate compounds may have a larger gap than our predicted ones.

To further elucidate the nature of the electronic band structure, we have calculated total density of states (TDOS) and partial density of states (PDOS) of ammonium nitrate and sodium nitrate, as shown in Figs. 5 and 6 respectively. The overall TDOS and PDOS profiles are moderately in

Table 2 Calculated and theoretical equilibrium structural parameters for sodium nitrate

Parameters	This work
Bond lengths (Å)	
N1–O1	1.210
Na1–O1	4.221
Na1–N1	4.110
Bond angles (deg)	
O1–N1–O2	123.3
O1–N1–Na1	93.1

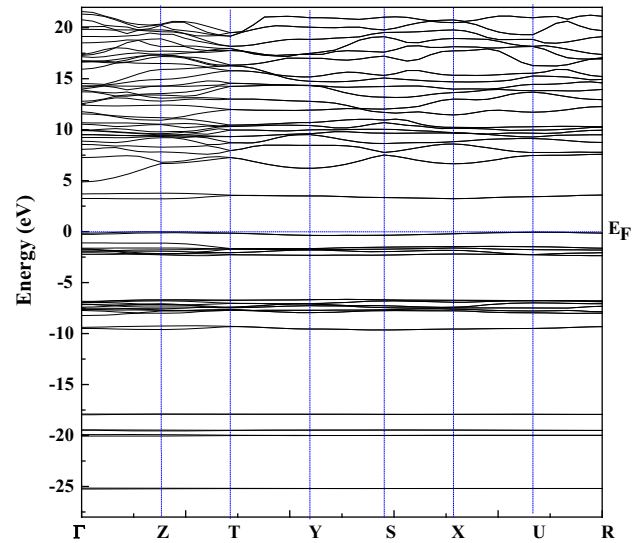


Fig. 3 Band structure for high-symmetry directions in the Brillouin zone of ammonium nitrate IV

good agreement with previous theoretical results [10, 19, 20].

For ammonium nitrate IV, the lower part of the valence band (VB) located between -26 and -17.4 eV is dominated by the N1(2s) and O(2s) states with a small

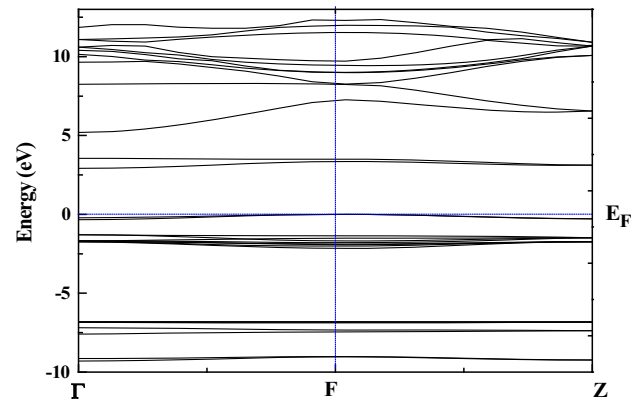


Fig. 4 Band structure for high-symmetry directions in the Brillouin zone of sodium nitrate

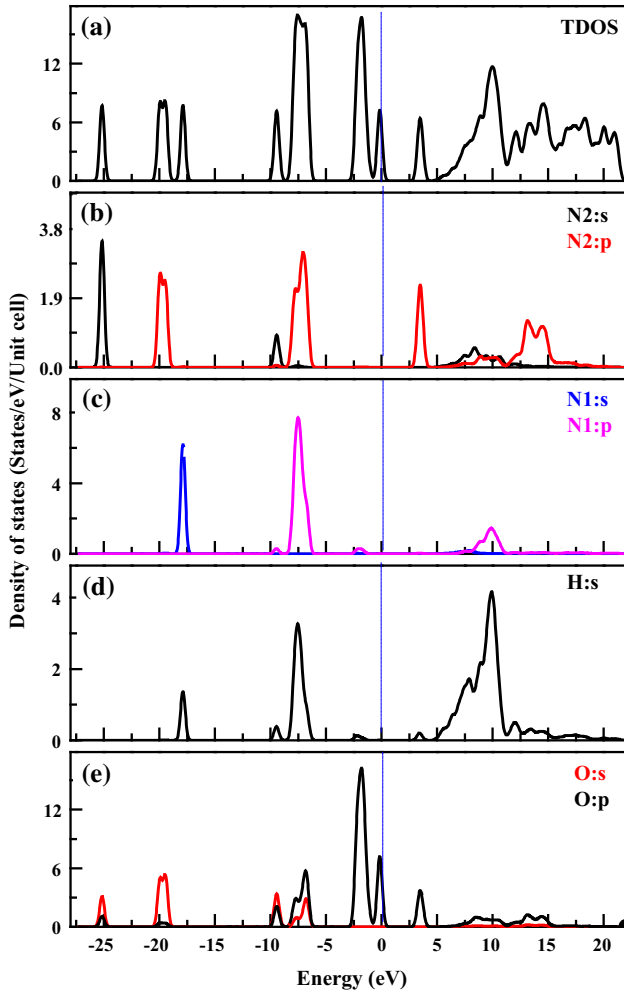


Fig. 5 (a) Calculated total density of states (TDOS) of ammonium nitrate IV. (b)–(e) Partial density of states (PDOS) for N2 of nitrate group, N1 of ammonium, H, O atoms

contribution from N2(2p), N2(2s) states and a much smaller contribution from H(1s) and O(2p) states. The top of the valence band (−10.2 to −6.1 eV) and (−2.7 to −0.8) represents a mixing of both ammonium and nitrate ions states, which explain the molecular character of ammonium nitrate IV as exhibited by Sorescu et al. [10]. The band around −2 eV is formed mainly from the O(2p) and a very small contribution of ammonium N1(2p) states. Above the Fermi level (3–4 eV), the conduction band (CB) is formed by both N2(2p) and O(2p) states of the nitrate ions. Over 6 eV, the mixing occurs between N1(2p), N2(2s), O(2p) and H(1s) states.

For sodium nitrate, the lower part of the valence band (VB) extended in the range (−10 to −6.4 eV) is dominated by O(2s) and O(2p) with a small contribution from N(2s) and N(2p) states. The top of the valence band is represented by the O(2p) character. As a result, the mixing of states within the nitrate group confirm the molecular

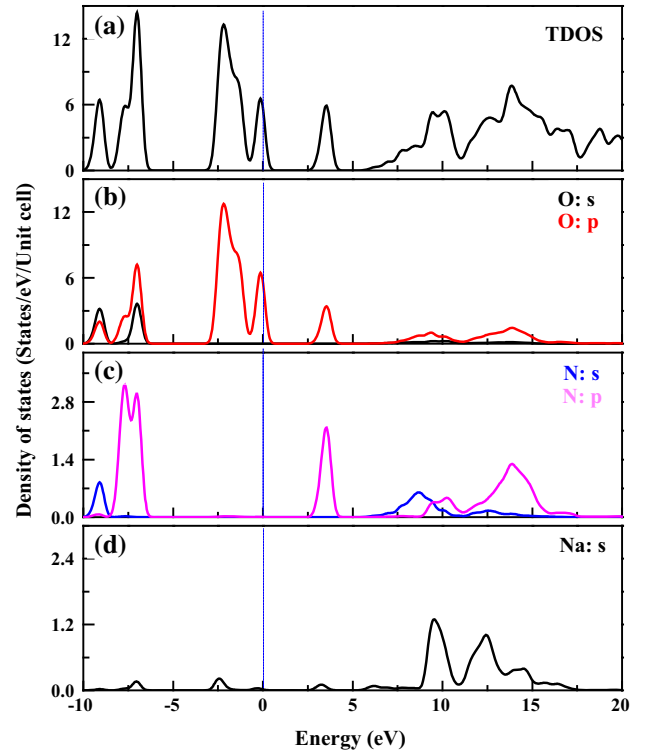


Fig. 6 (a) Calculated total density of states (TDOS) of sodium nitrate. (b)–(d) Partial density of states (PDOS) for O, N, Na atoms

character of this crystal as shown previously [19, 20]. Above the Fermi level, the conduction band (CB) is dominated principally by N(2p) and O(2p) states in the range of 2.5–4.5 eV. More than 5 eV, this region is dominated by Na(3s), N(2p) and O(2p) plus small contribution of N(2s) states.

3.3. Optical properties

The complex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ of ammonium nitrate IV and sodium nitrate is shown in Figs. 7 and 8 respectively. The calculations are performed for three polarization cases [100], [010] and [001] for ammonium nitrate. The behaviour of $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ is similar for [100] and [001] directions compared to [010] case. The imaginary part $\varepsilon_2(\omega)$ of the dielectric function is directly connected with the energy band structure and proportional to the optical absorption spectrum of NH_4NO_3 IV. $\varepsilon_2(\omega)$ in Fig. 7(b) has very similar form along the two directions [100] and [001] with a sharp and intense peak centered around the same energy value, whereas, the spectrum of [010] case is located in the same range of energy but with weak intensity. Ammonium nitrate IV crystal absorbs the radiation whose energy lies within the energy interval between 3.5 eV and 16.5 eV. The analysis of $\varepsilon_2(\omega)$ of this crystal together with characterization of the

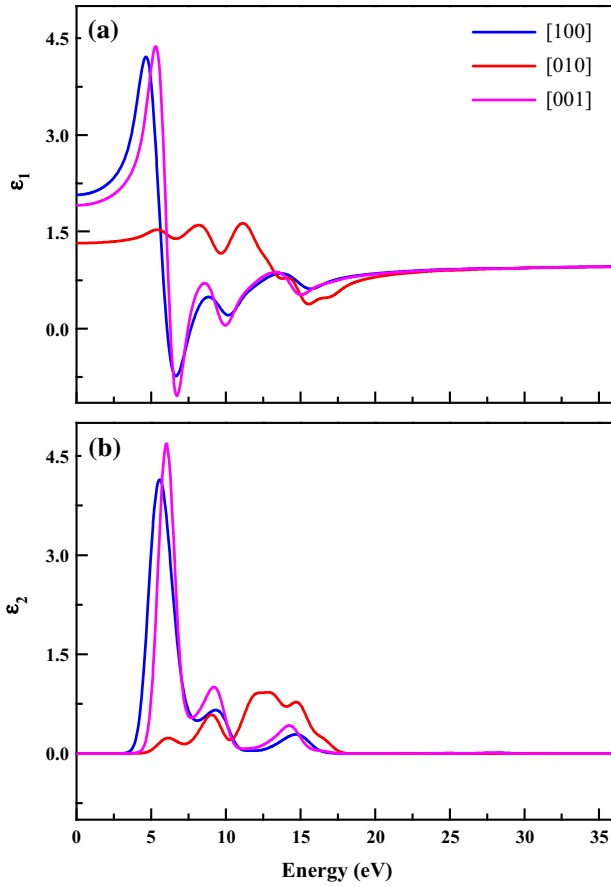


Fig. 7 (a) Real $\varepsilon_1(\omega)$ and (b) imaginary $\varepsilon_2(\omega)$ parts of dielectric function as a function of photon energy for ammonium nitrate IV

electronic structure reveals that the major absorption occurs due to the transition from the occupied O(2p) to unoccupied N(2p) states.

The dielectric function spectra for polarized light of sodium nitrate along the perpendicular ([100] direction) and parallel ([001] direction) to c -axis are presented in Fig. 8(a, b). For the two directions $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ behaviour is rather analogous with some differences in details. The imaginary part $\varepsilon_2(\omega)$ in Fig. 8(b) has similar form along the two directions with some differences in the intensities. Sodium nitrate crystal absorbs the radiation of energy between 3 and 20 eV. The main absorption band is dominated by the transition from O(2p) to O(2p) and N(2p) states as determined from the PDOS analysis.

Figures 9 and 10 exhibit the variation of the calculated refractive index $n(\omega)$, extinction coefficient $k(\omega)$, reflectivity $R(\omega)$ and energy-loss spectrum $L(\omega)$ in relation with the energy of incident radiation for the two crystals. The extinction coefficient directly describes the attenuation of electromagnetic waves within the material. This coefficient has larger value in the range of wavelength from 75 to

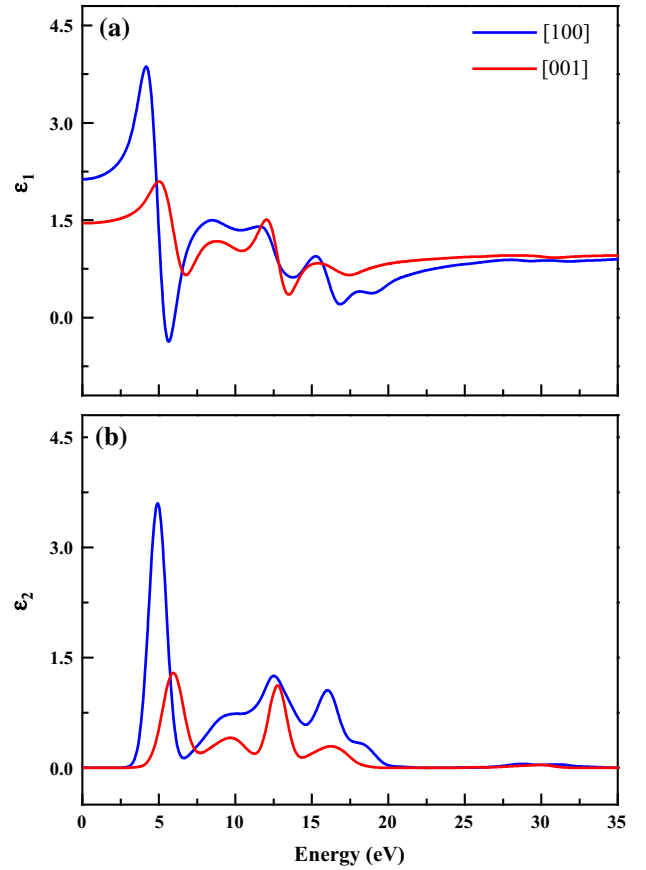


Fig. 8 (a) Real $\varepsilon_1(\omega)$ and (b) imaginary $\varepsilon_2(\omega)$ parts of dielectric function as a function of photon energy for sodium nitrate

350 nm for ammonium nitrate IV [see Fig. 9(b)] and from 60 to 380 nm for sodium nitrate [see Fig. 10(b)], where the materials mostly absorb. Our results are in agreement with the available data [18, 36]. From Fig. 9(a), the calculated refractive indices $n(\theta)$ for AN IV are 1.44, 1.12 and 1.38 for [100], [010] and [001] directions respectively. Our values corroborate with the existing ones [36]. In the sodium nitrate case, the corresponding values of $n(\theta)$ are 1.44 and 1.20 along the perpendicular and the parallel to c -axis [see Fig. 10(a)]. As exposed in Figs. 9(c) and 10(c), the maximum reflectivity value is reached at 6.8 eV in the [100] and [010] directions for ammonium nitrate and around 5.9 eV in the sodium nitrate case. The energy-loss spectrum describes the energy-loss of a fast electron traversing the material. For ammonium nitrate, the peaks of the energy-loss spectrum are at about 7.6 and 10.2 eV for [100] and [001] directions respectively and at 15.7 eV for [010] case as shown in Fig. 9(d). From Fig. 10(d), the peaks are located at about 6.1 and 17.2 eV along the perpendicular to c -axis and at 13.5 eV along the parallel to c -axis for sodium nitrate.

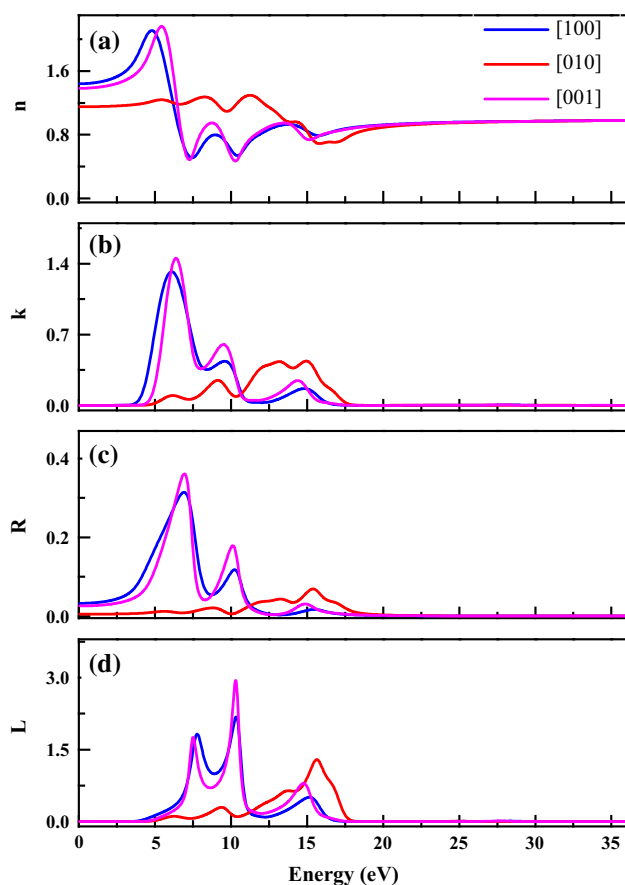


Fig. 9 Calculated optical properties of ammonium nitrate IV: (a) Refractive index (n), (b) extinction coefficient (k), (c) reflectivity (R) and (d) energy-loss spectrum (L)

4. Conclusions

In summary, we have calculated the electronic and the optical properties of ammonium nitrate IV and sodium nitrate crystals using plane-wave ab initio calculations based on density function theory and the pseudo-potential method. Our structural parameters are in good agreement with previous theoretical published values and experimental data. The electronic structures reveal that ammonium nitrate IV has a direct band gap of 3.21 eV and sodium nitrate has an indirect band gap of 2.92 eV.

The optical constants such as, the dielectric function, refractive index, extinction coefficient, reflectivity and energy-loss function are also calculated. This study shows that ammonium nitrate and sodium nitrate absorb radiation in the ultraviolet range. Furthermore, for both crystals the 2p states of the nitrate moiety play a major role in these optical transitions as initial and final states.

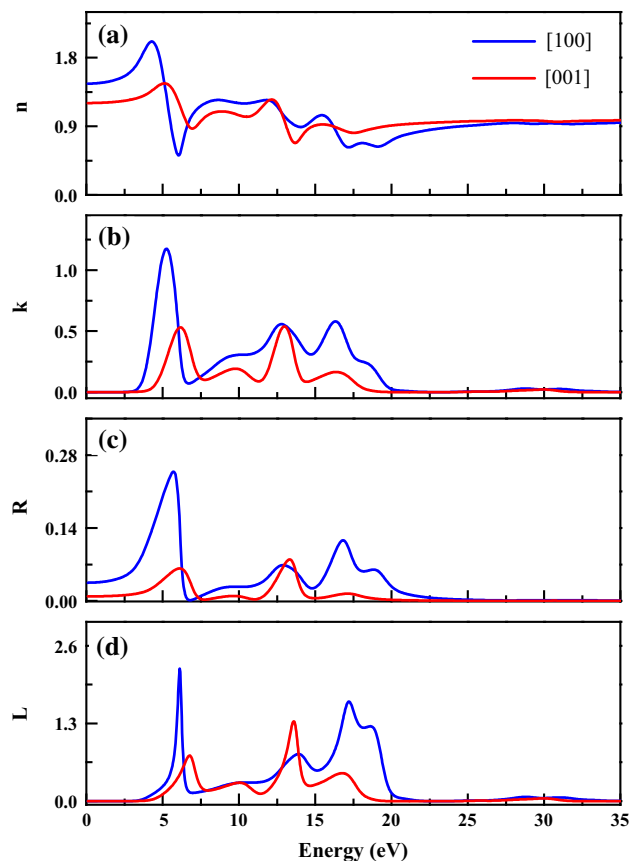


Fig. 10 Calculated optical properties of sodium nitrate: (a) Refractive index (n), (b) extinction coefficient (k), (c) reflectivity (R) and (d) energy-loss spectrum (L)

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