

PHYSICAL PROPERTIES INVESTIGATION USING AB INITIO MOLECULAR DYNAMICS METHODS : APPLICATION TO AMMONIUM NITRATE

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ABSTRACT

Physical properties of crystalline ammonium nitrate (AN), phase IV, stable between 255 and 305K, have been investigated using molecular dynamics method coupled with ab initio calculations based on density function theory and the pseudopotential approximation. The optimizations of the crystal structures have been done with full relaxation of the atomic positions and lattice parameters under the experimentally determined crystal symmetries. Periodic boundary conditions are used, with the occupied electronic orbitals expanded in a plane-wave basis. The predicted crystal structure was found in good agreement with that determined experimentally by neutron diffraction data. Molecular dynamic simulations have been performed to predict average equilibrium properties of the lattice at finites temperature and pressure. The crystal volume is compressed by 70% of the equilibrium volume in the pressure range 0-600 GPa. However, for different temperatures tested no significant volume changes were found. The large charge redistributions of the NH_4^+ and NO_3^- ions seen as a result of lattice compression indicate a decrease of the ionic character of the crystal and a concomitant increase of the covalent character. Band structure calculations indicate an insulator character of AN with a band gap of 3.37 eV. The increase in pressure induces a decrease of the band gap by about 40%. The nitrate ion exhibits a characteristic UV absorption spectrum consisting of a strong band around 180 nm and a considerably weaker absorption around 300 nm.

Keywords: Ab initio; molecular dynamics; Ammonium nitrate; aerosols

1 INTRODUCTION

Ammonium nitrate (AN) material has been widely used as fertilizer, blasting agent and in solid oxidizers fields for rocket propulsion. Ammonium nitrate is one of the most important constituents of atmospheric aerosols and accounts for 10–30% of the fine aerosol mass [1]. The importance of AN in atmospheric aerosols is expected to increase significantly in the future [2,3,10]. Nevertheless, atmospheric aerosols are concerned by several atmospheric processes and environmental pollutions. Due to their chemical composition, especially when mixed with polluted air rich in SO_2 and NO_x ,

these aerosols can produce acid rain, which causes structural erosion and degradation of soil and water quality. Because of their interaction with electromagnetic radiation, aerosols also impair visibility. In addition the aerosols influence the climate forcing through direct and indirect mechanisms. Direct forcing is the effect induced by scattering and absorption of solar radiation from the particles themselves. Indirect forcing is the effect of aerosols on cloud optical properties, lifetime and Aledo, caused by alteration of the available cloud condensation nuclei (CCN).

The knowledge of fine particles properties is of great importance to improve our understanding of atmospheric processes involved in local and global environment problems.

Nitrate ammonium can exist in five known polymorphic forms (phases V, IV, III, II and I) under normal pressure and temperature range of 0-442K. The phase IV of AN (AN-IV) is stable from 255 to 305K, and is the only phase considered in current atmospheric chemical models [7,8]. However, the role of AN as atmospheric aerosol requires a particular exploration at different levels. In this paper, we provide a description of structural, electronic and optical properties of AN-IV, by the exploitation of simulation tools at various conditions.

2 COMPUTATIONAL DETAILS

The CASTEP (Cambridge Serial Total Energy Package) software package has been used to perform the present calculations. This program evaluates the total energy of periodic systems based on ab initio density-functional theory and the pseudopotential approximation. Periodic boundary conditions are used, with the occupied electronic orbitals expanded in a plane-wave basis. A gradient corrected form of the exchange correlation functional (GGA) was exploited.

Molecular dynamics simulations are performed at finite temperature and pressure (NPT) through further tests of the intra- and intermolecular potentials. We have opted for the Nosé-Anderson-Barostat implementation to explore the AN-IV molecular ionic crystal properties at various temperatures and pressures in the ranges 255-305 K and 0-600 GPa. The equations of motion for the ions and the simulation cell are incorporated through the Verlet Leapfrog method [6]. The model system involves a simulation box of 3 x 3 x 3 crystallographic unit cells.

1- For the Geometry optimization under experimental space group symmetries, the relaxation of the unit cell was done with respect to lattice parameters a , b and c and fixed angles $\alpha = \beta = \gamma = 90$. Within these calculations the sampling k -points were generated using the Monkhorst scheme with mesh box parameters 2 x 3 x 3 along the three reciprocal lattice vectors.

2- Optimizations of geometrical parameters over 0-600 GPa were performed in space group P1 to allow structural relaxations of all crystallographic parameters.

3- For NPT molecular dynamic simulations, the system was equilibrated to the lowest temperature configuration and atmospheric pressure.

3 RESULTS AND DISCUSSION

3.1 Structure at ambient pressure

The crystal structure of AN-IV has been illustrated accurately by neutron diffraction [4] and X-ray [5] studies. It has an orthorhombic structure, with space group $Pmmn$ and two NH_4NO_3 formula units per unit cell as shown in figure 1. A two-dimensional infinite network of hydrogen bonds between the N-H atomic pairs of the ammonium group and the O atoms of the nitrate exists in planes parallel to (001) with the adjacent molecular sheets connected by van der Waals forces.

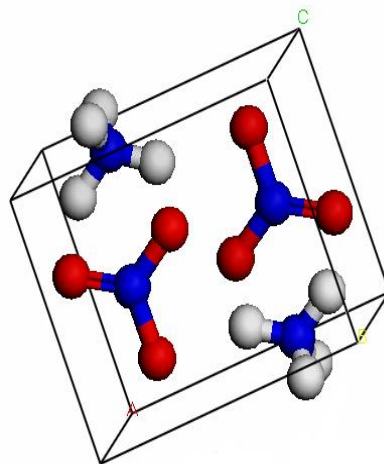


Figure 1. Crystal structure of AN-IV (N:blue, O:red, H:gray)

The analysis of geometrical parameters given in Table 1 shows a good agreement between the calculated and the experimental values, with maximum deviations from the experimental data of 3.59% [4] and 2.98% [5]. Our calculations confirm that the N-O1 bond length is longer than N-O2 as seen experimentally [4, 5]. This is attributed to the fact that O1 atoms are involved in strong hydrogen bonds while O2 is not [4]. Accordingly, distances N-H1---O1 and N-H2---O1 are shorter than N1-H1---O2. The superposition of these types of interactions determines the existence of infinite hydrogen-

bonded chains formed by N1-H1---O1---H1-N1 bonds [6].

Table 1. Comparison of the calculated and experimental of relevant parameters for AN-IV

	calc	Exp[4]	Exp[5]
Bond lengths (Å)			
N2-O1	1.2948	1.274	1.268
N2-O2	1.2597	1.254	1.230
N1-H1	1.0374	1.069	
N1-H2	1.0335	1.072	
Hydrogen bonds (Å)			
N1-H1---O1	2.0263	2.050	2.042
N1-H2---O1	2.0994	2.161	2.164
N1-H1---O2	2.3051	2.326	
Bond angles (°)			
O1-N2-O2	118.9	120	119.9
O2-N2-O3	122.1	120	120.3
Total Energy (eV)	28711.12		

3.2 Structural and electronic Properties at high pressure

The compressibility of AN-IV has been investigated for the pressure range 0-600 GPa. The unit cell volume as a function of pressure is presented in Figure 2. It has been found that over this pressure range the crystal volume is compressed by 70% of the equilibrium volume, with 50% noted for pressures less than 100 GPa. This behavior can be understood as being due to an increase of the charge overlap and a change of the bonding character toward a covalent one [6]. The unit cell volume estimated at 0 GPa is in good conformity with the experimental value ($V_{0 \text{ exp}} = 153,99 \text{ \AA}^3$), it deviated of only 1.5%.

Band gap values have been determined from the band structures for optimized structures of AN-IV at different pressures tested. The results are illustrated in figure 3. Band structure calculations indicate that AN-IV is an insulator with a band gap of 3.37 eV. The increase in pressure beyond 100 GPa induces a decrease of the band gap by about 40%, it attained a minimum of 2.0 eV at 600 GPa. This change seems being a result of a modification of conduction property from insulator to a metallic system.

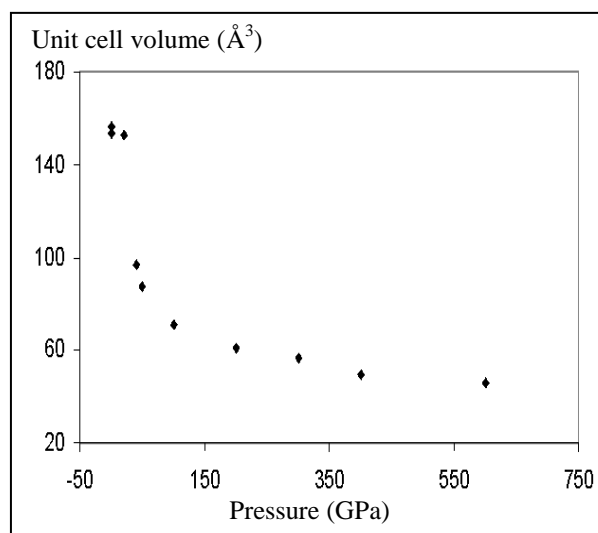


Figure 2. Variation of the unit cell volume of AN-IV crystal as a function of pressure

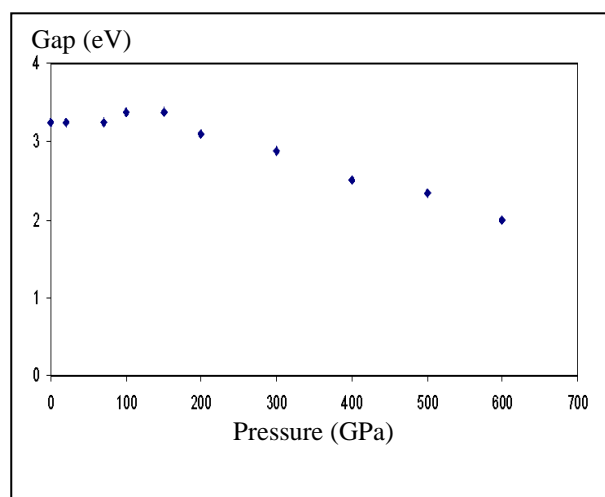


Figure 3. Variation of the AN-IV band gap as a function of pressure

An unconventional approach to describe the effect of charge rearrangement caused by compression of the lattice can be obtained by evaluation of the Mulliken charges of different atoms of the system. The Mulliken charges can provide only a qualitative description of the bonding characteristics. The variations of the individual atomic Mulliken charges as functions of pressure are shown in Figure 4. We observe that the variation of charges increases for ammonium nitrogen atoms and decreases for those in the nitrate ions with increasing pressure. These changes take place together with a decrease in H atoms charges and a significant increase of the charge on the O atoms of the nitro groups involved in hydrogen bonding (O1 atoms).

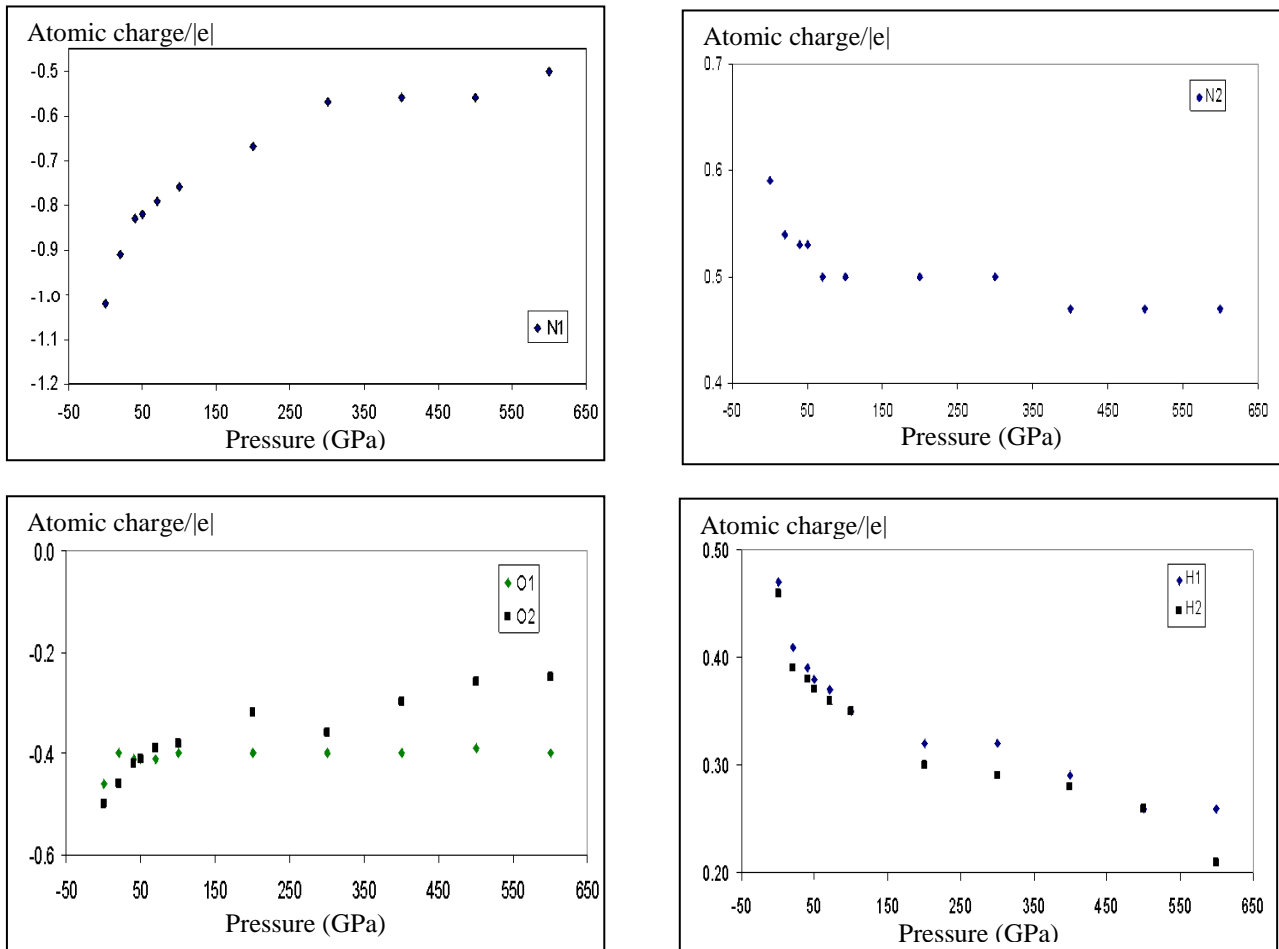


Figure 4. Variation of Mulliken charges attributed to different atoms of NH_4^+ and NO_3^- ions in AN-IV as a function of pressure

The large charge redistributions seen as a result of lattice compression indicate a decrease of the ionic character of the crystal and a simultaneous increase of the covalent character

3.3 Temperature effects on structural and optical properties

In this section, we carry out our simulations by considering the molecular motion as a function of temperature and pressure. This approach provides more realistic tools to predict materials behaviors and properties.

For this purpose, the temperature dependencies of the structural lattice parameters and the unit volume cell have been explored by performing isothermal isobaric molecular dynamics simulations at atmospheric pressure between 255 and 305 K. The main results are illustrated in figure 5 (a, b). As we can notice, no significant changes are obtained over 50°C for all the parameters. The variation remains small, not more than 10% for the unit volume cell.

The optical properties are important and very useful quantities in many applications. Providing optical constants for multi component aerosols will be of great efficacy to high-spectral resolution IR remote sensing as well as radiative balance analysis in climate studies [9]. The absorption and refractive indices can precisely define the full optical behavior of the material under investigation [9, 11]. Absorption and reflectivity coefficients calculations were performed at 270K for 10^{-4} and 10^{-7} GPa, corresponding to pressure limits of the troposphere. Spectra of AN-IV light absorption and reflectivity are reported in figures 6 and 7 respectively. The AN crystal exhibits a characteristic UV absorption spectrum consisting of a strong band around 180 nm and a considerably weaker absorption around 300 nm. The reflectivity coefficient seems insignificant. This first result confirms experimentation [3], ammonium nitrate is implicated in photochemistry processes.

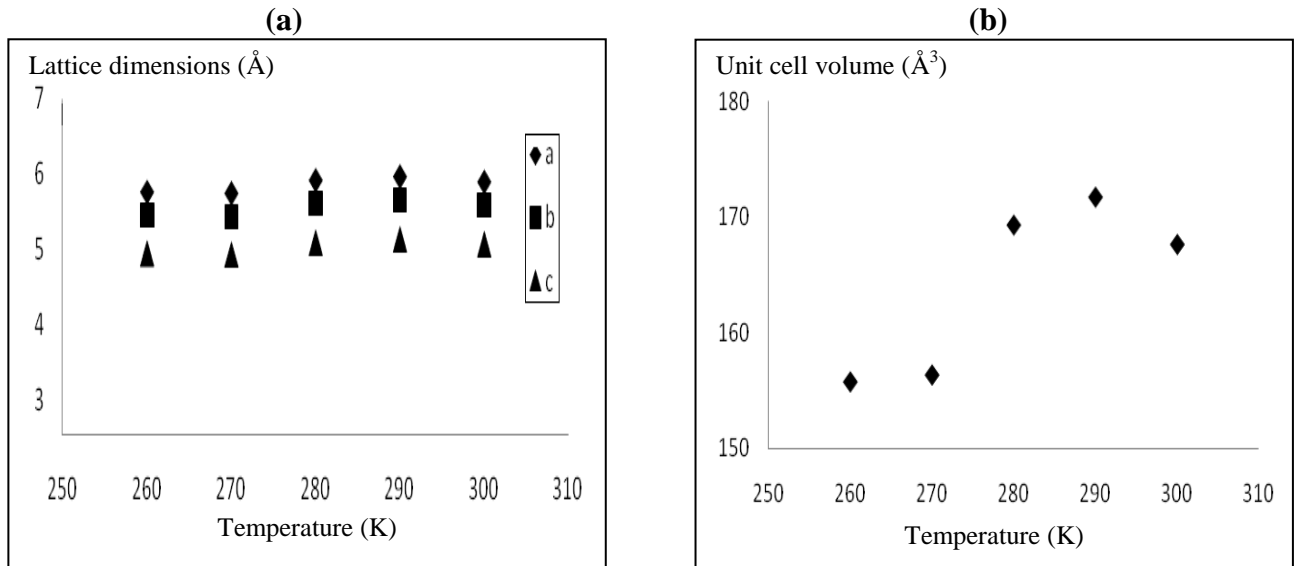


Figure 5. Variation of the lattice dimensions and the unit cell volume of AN-IV crystal as a function of temperature

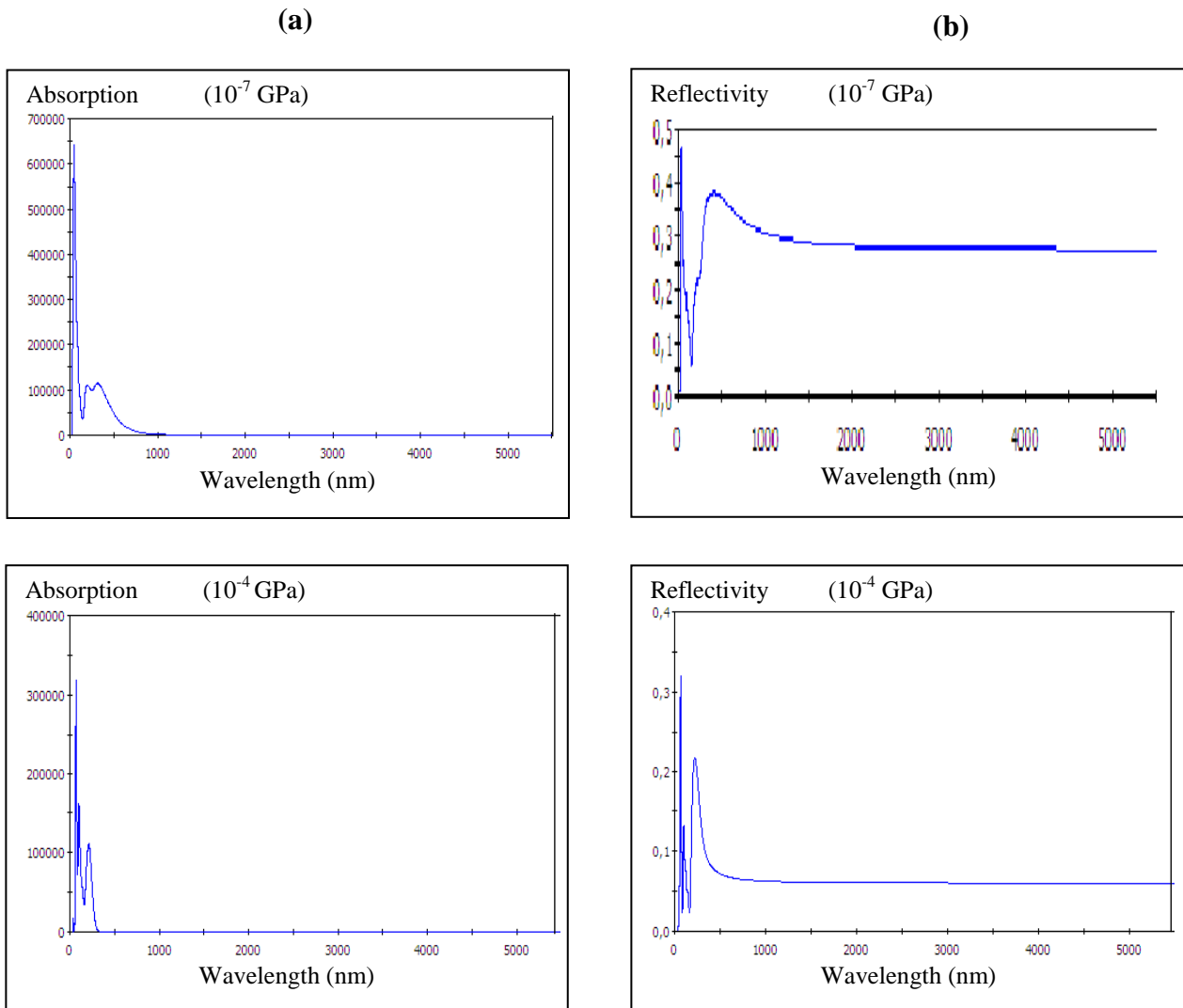


Figure 6. Optical parameters spectra: (a) Absorption (b) Reflectivity

4 CONCLUSION

In conclusion, we summarize the main points of the work as follows:

The geometrical characteristics of the AN-IV are well reproduced by our calculations and are in excellent agreement with the structural configurations determined experimentally.

The increase of pressure from 0 to 600 GPa affects strongly the structural and electronic parameters. AN-IV volume is compressed by 70% related to the charge reorganization and a modification of the bonding nature.

The structural parameters of AN-IV at normal pressure are not affected by temperature increases. Its stability is confirmed as atmospheric aerosol.

The first optical parameters results affirm that AN-IV alters visibility by a strong absorption to the short wave and visible.

More spectral and optical analysis of AN in a mixture and at different physical states and may inform us

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