Study of the structural, vibrational and thermodynamic properties of natroxalate mineral using density functional theory

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ABSTRACT

Natroxalate mineral, $Na_2C_2O_4$, is a fundamental oxalate mineral widespread in nature, present in humans, animals and plants, as well as in naturally occurring minerals. The characterization of oxalate minerals is extraordinarily important since these organic minerals are indicators of environmental events and of the presence of biological activity, because they are commonly of biological origin. These minerals are currently under study to investigate the possible biological activity on Mars. The identification of these compounds is usually performed by X-ray diffraction and Raman spectroscopy. Theoretical calculations are of great value for the study and interpretation of the results of these experimental techniques. In this work, natroxalate mineral structure and Raman spectrum was studied by first principle calculations based on the density functional theory. The computed structure of natroxalate reproduces the one determined experimentally by X-ray diffraction (monoclinic symmetry, space group $P2_1/c$; lattice parameters a = 3.449 Å, b = 5.243 Å; c = 10.375 Å). Lattice parameters, bond lengths, bond angles and X-ray powder pattern were found to be in very good agreement with their experimental counterparts. Raman spectrum was then computed by means of density functional perturbation theory and compared with the experimental spectrum. Since the results were also found in agreement with the experimental data, a normal mode analysis of the theoretical spectra was carried out and used in order to assign the main bands of the Raman spectrum. The band found at about $567 \, cm^{-1}$, described as a single peak in previous experimental works, is shown clearly to have two contributing bands. Finally, two bands of the observed spectrum, located at the wavenumbers 1750 and $1358 \, cm^{-1}$, were not found in the theoretical spectrum. This is because these bands correspond to an overtone, $2\nu_1$ (ν_1 = $875 \, cm^{-1}$), and a combination band, $\nu_1 + \nu_2$ (ν_1,ν_2 = 875, $481 \, cm^{-1}$), respectively. Finally, the fundamental thermodynamic properties of natroxalate mineral were determined. The calculated specific heat at $298.15 \, K$ is in excellent agreement with the experimental value, the difference being less than 1%. Since for most of these properties there are not experimental values to compare with, their values were predicted.

1. Introduction

Organic minerals have been recognized since the early stages of modern mineral science [1]. Most of these minerals are formed by inorganic processes, but it is increasingly recognized that minerals may also be produced organically. The recognition of the materials formed in this way has opened a new area of research, biomineralization, which is the study of the processes by which organisms produce minerals [2]. Because the occurrence of organic minerals is associated to high concentrations of certain organic compounds in natural environments, the study of the origin and formation processes of these minerals will lead us to understand the behavior of the organic molecules in the environment.

Oxalate minerals are fundamental organic minerals widespread in

nature, present in humans, animals and plants [3–14], as well as in naturally occurring minerals [15,16]. The characterization of oxalate minerals is extraordinarily important since these minerals are indicators of environmental events, such as climate change [17], and of the presence of biological activity, because they are commonly of biological origin [2]. Evidence for the existence of primitive life forms like lichens and fungi can be based upon the formation of oxalates. These minerals form as the result of expulsion of heavy metals from fungi, lichens and plants [9–12], since these organisms can control their heavy metal intake through expulsion of metal salts such as oxalates. The production of simple organic acids as oxalic and citric acids has profound implications for metal speciation in biogeochemical cycles [12]. The presence of oxalates can be used as a marker for the pre-existence of life.

These minerals are currently under study to investigate the possible biological activity on Mars [18–27]. The study of the formation, transport, and concentration of oxalate in the extremely arid zones may provide a geochemical analogue for oxalate-bearing minerals recently suggested to exist on Mars [18]. If life existed on Mars at some time in the past, or even exists in the present time, low life forms such as fungi and lichens could exist. These organisms may be found in very hostile environments [6–8]. Raman spectroscopy has been selected as one of the main analytical instruments for the ExoMars mission [19,20] to identify the geological and biogeological spectral signatures that could confirm the presence of oxalates in Mars. While there have been no inambiguous detections of specific organic compounds on Mars, meteoritic and cometary material is continuously delivered to the surface of Mars, and oxalic acid is the most abundant dicarboxylic acid in several chondrites [28–30]. Based on X-ray diffraction and reflectance spectroscopic analyses, Applin et al. [26,27] have shown that solid oxalic acid and its most common mineral salts are stable under the pressure and ultraviolet irradiation environment of the surface of Mars. Therefore, oxalate minerals could be important in numerous Martian geochemical processes, acting as a possible nitrogen sink, and/or contributing to the formation of organic carbonates, methane, and hydroxyl radicals [26].

The presence of oxalates has been evidenced by the deterioration of works of art [31–37]. Carbon dating of oxalic acid enables estimates of the age of the works of art [38]. Such minerals are also important in human physiology because these minerals are also found in the urinary system in the human body [3–5]. Oxalates are also used in industry [39–44]. For example, oxalates are major intermediates in many advanced oxidation processes for treating organics [40–43]. Sodium oxalate serves as a metal cleaning preparation in the textile, leather and tanning industries and it is also used in analytical and solvent extraction chemistry. For example, sodium oxalate is used as primary volumetric standard for manganometry and acidimetry [44].

The identification of these compounds is usually performed by X-ray diffraction and Raman spectroscopy. Theoretical calculations are of great value for the study and interpretation of the results of these experimental techniques since they may be used to resolve the main uncertainties encountered. The use of infrared and Raman spectroscopy for the study of oxalates originated with the necessity to study renal stones [45,46]. Vibrational spectroscopy has been extensively used to the study of oxalates [21–25,47–55] and many synthetic oxalates have been also studied [54,55]. Oxalates are most readily detected using Raman spectroscopy. Since most Raman spectra of oxalate minerals are mutually exclusive, these minerals may be adequately recognized with this kind of spectroscopy [21–25]. Therefore, Raman spectroscopy has the potential to identify the existence or pre-existence of life forms on planets such as Mars [21]. The minerals on Earth-like planets may be explored by robotic devices, which carry portable Raman spectrometers with possible fibre optics to collect spectral data.

The structure of natroxalate mineral phase has been determined by experimental X-ray diffraction techniques [56,57] and theoretical calculations [58,59]. In this paper, we performed a complete structural characterization of natroxalate by theoretical solid-state methods that agree very well with the structure obtained experimentally [56] and improves the one obtained theoretically [58]. Also, although the Raman spectrum of this mineral has been determined by experimental methods [21–23], a precise assignment of the main bands in the spectra is lacking. While the Raman spectrum of natroxalate was studied by Lakkaraju et al. [60] using DFT calculations of gas-phase clusters, these authors determined only two Raman bands, their assignment being taken from the experimental works. Therefore, a complete solid-state computation of the Raman spectrum of natroxalate mineral was carried out in this paper, including the computation of intensities and the assignment of all the observed bands. We have performed a complete assignment of the experimental vibrational

Raman bands since theoretical methods provide detailed views at the microscopic scale of the atomic vibrational motions in the corresponding normal modes. Finally, the fundamental thermodynamic properties of natroxalate mineral were determined. Since, as far as we know, the values for most of these properties of this mineral have not been determined by using either experimental or theoretical methods, their values were predicted in this work. Computations were carried out by means of Density Functional Theory [61] (DFT) based on plane waves and pseudopotentials [62]. The same methodology used successfully in previous works [63–67] was employed.

2. Methods

2.1. Geometries and Raman spectrum

CASTEP code [68], a module of the Materials Studio package [69], was employed to model natroxalate structure. The generalized gradient approximation (GGA) together with PBE functional [70] and Grimme empirical dispersion correction, called the DFT-D2 approach [71], were used. The introduction of dispersion corrections improved significantly the computed structural and vibrational properties as a result of the better description of non-bonded interactions among the atoms within the unit cell. The pseudopotentials used for C, O and Na atoms in the unit cell of natroxalate mineral were standard norm-conserving pseudopotentials [72] given in CASTEP code (00PBE-OP type).

Geometry optimization was carried out by using the Broyden–Fletcher–Goldfarb–Shanno optimization scheme [62,73] with a convergence threshold on atomic forces of 0.01 eV/Å. The kinetic energy cut-off and k-point mesh [74] must be selected to ensure good convergence for computed structures and energies. Natroxalate structure was optimized in calculations with increasing complexity by increasing these parameters. The optimization performed with a cut-off of 900 eV and a K mesh of $6 \times 4 \times 2$ (12 K points) gave a well converged structure that was used to determine the final results. Nevertheless, to show the convergence of the calculations, we have also included the structural results of the calculations with a large K mesh of $7 \times 5 \times 3$ (33 K points).

For the calculations of vibrational properties, the linear response density functional perturbation theory (DFPT) [75–77] implemented in the CASTEP code was used in the same way as in previous works [63–67]. Phonon frequencies at the gamma point of the Brillouin zone were computed using atomic displacement perturbations. Raman intensities are third-order derivatives of total energy with respect to vibrational mode (atomic position) and laser field (electric field, twice). These are calculated in CASTEP [68] by using a combination of perturbation theory (second derivative with respect to field) and finite differences (third derivative with respect to atomic displacement). Therefore, a combination of the DFPT and finite difference techniques are used in order to determine the Raman spectrum. The frequencies presented in this work have been scaled to correct for anharmonicity and remaining errors of the theoretical treatment employed, such as incomplete treatment of electron correlation and basis set truncation [78]. The scale factor used was 1.0363 and it was selected in order to adjust as far as possible the calculated Raman spectrum to the experimental one.

All the results reported in this work were obtained imposing monoclinic space symmetry (space group $P2_1/c$). However, the geometry optimization and vibrational calculations were also performed without symmetry restrictions. The results obtained in these last calculations were essentially the same as in the calculations in which the symmetry restrictions were imposed.

2.2. Thermodynamic properties

The methods employed for the calculation of thermodynamic properties of natroxalate were the same as in our previous works