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First principle investigation of the mechanical properties of natural layered nanocomposite: Clinochlore as a model system for heterodesmic structures

Gianfranco Ulian, Daniele Moro, Giovanni Valdrè*

Centro di Ricerca Interdisciplinare di Biomineralogia, Cristallografia e Biomateriali, Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università degli Studi di Bologna, Piazza di Porta San Donato 1, 40126 Bologna, Italy

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ABSTRACT

For many technological applications, it is of paramount importance to study the mechanical behaviour of heterogeneous multi layered materials, and how they develop at the nanoscale. By employing a nature-based approach (*learning from Nature*) and *ab initio* Density Functional Theory (DFT) methods, in the present work we report a detailed mechanical investigation of a very interesting natural heterodesmic nanocomposite material made of alternated stacked magnesium hydroxide (brucite-like) and hydroxysilicate (talc-like) layers. This mineral phase has very interesting surface and bulk crystal-chemical properties, but its elastic behaviour is still not well known. Both the hydrostatic compression and the second order elastic constants were reported. An ideal, stoichiometric structure and a cation-substituted one were considered to stress the power of DFT methods in tailoring the properties, and the results were presented and consistently discussed with the experimental data available in literature. This study showed that the DFT/B3LYP-D* approach represents a powerful route to investigate other layered structures of multilayer composites for tailoring of specific mechanical properties.

1. Introduction

In recent years, there is a growing interest on layered materials and composites, whose structural, electronic and mechanical properties could be extremely helpful in their technological applications. One of the most investigated in the last decade is graphene, a single-layer structure presenting very different properties from its bulk counterpart, the mineral graphite [1]. This pioneer research paved the road to the synthesis and investigations of other single-layered materials extracted, for instance, from boron nitride [2] and silicon carbide [3]. In addition, several researches are now focused also on the possibility of realizing nanocomposite structures made of alternated single-layered materials [4–6].

Nature spontaneously provides composite materials, for example, several minerals present a macro- to nanocomposite structure. Among the silicate minerals, the phyllosilicate subclass is composed by naturally occurring stacked layers of hydroxysilicates, made of sheets of both silica tetrahedra bonded to octahedrally-coordinated divalent or trivalent cations (principally magnesium and aluminium). The layers (presenting strong covalent bonds) are held together by different forces (hydrogen bonds, electrostatic and/or van der Waals), depending on the chemistry of the mineral (heterodesmic structures).

The interest on phyllosilicates minerals as composite materials grew in the last decades, as they are used today in several fields. To cite some examples, in the polymer industry, talc is an appreciated material to realize both organic/inorganic co-polymers (composite materials) with tailored properties, in particular increased strength [7,8], and current researches are focused on its possible employment in geopolymers for structural applications [9,10]. In addition, their almost atomically flat surfaces make them ideal substrates in biotechnological applications, such as to control the adsorption of biomolecules, from single molecules [11] to larger macromolecules [12–15].

All the cited applications of phyllosilicates need a detailed knowledge on both how the mineral interacts with the environment and their mechanical properties. For this reason, it is of paramount importance to characterize the mechanical stability, the morphology, the chemical composition, the presence of defective sites and the layer charge of these natural composites. These considerations can be obviously extended to all layered materials, both natural and synthetic.

In the present paper, clinochlore, an important member of the chlorite family, was chosen as a heterodesmic model system to investigate the elastic properties of natural composite materials. This mineral phase is a peculiar Mg-Al-hydroxysilicate, whose composite structure is made up of two structurally and chemically different layers of sub-nm thickness: the first is a magnesium hydroxide layer (also called brucite-like, B), 0.4 nm thick, given by magnesium/aluminium

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* Corresponding author.
E-mail address: giovanni.valdre@unibo.it (G. Valdrè).

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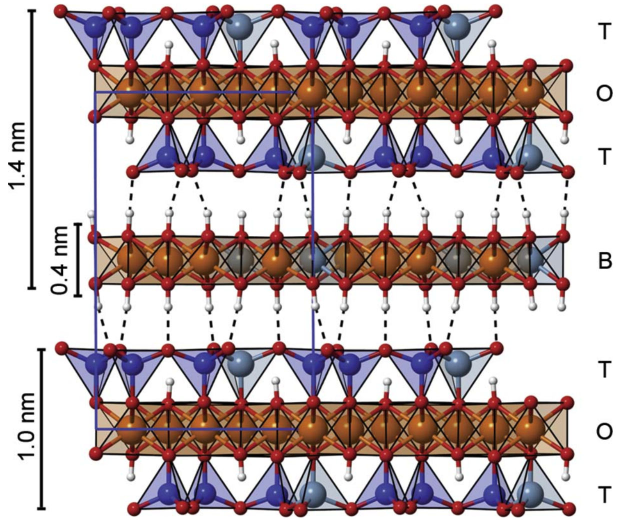

Fig. 1. View from the [0 1 0] direction of typical clinochlore mineral structure, with brucitic-type and talc-like layers labelled as B and TOT, respectively. The blue continuous line represents the mineral unit cell viewed along the [0 1 0] direction. Colour coding for atoms: blue – Si; cyan – Al; orange – Mg; red – O; white – H. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

cations in octahedral coordination with hydroxyl groups; the second is a hydroxysilicate layer (talc-like, TOT), 1 nm thick, composed of two tetrahedral sheets bound together by octahedrally-coordinated magnesium cations. These are the building blocks of clinochlore, which is made of alternated stacking of B and TOT layers, held together by hydrogen bonds. A graphical example of the clinochlore structure is reported in Fig. 1. Both silicon atoms of the tetrahedral sheets and magnesium cations can be partially substituted by aluminium atoms (in the talc-like and in the hydroxide layers). At the interface between the two layers the surface of monoclinic crystal system of the talc-like layer deforms to match the trigonal crystal system of the hydroxide one. The two layers present very different nanomechanical properties, surface electric potential and hydrophilicity/hydrophobicity, depending on both the type of the layer and the local stoichiometry of the mineral [16].

In recent studies, the surface properties of clinochlore were investigated [16], showing that it can adsorb, organize and self-assemble nucleotides and related macromolecules, RNA and DNA [14,17,18], and amino acids [11]. However, the knowledge on the mechanical stability of this natural material is somewhat limited to only few works [19–21].

The aim of the present work is two-fold: on first instance, the phyllosilicate nanocomposite elastic behaviour was investigated to fill this knowledge gap, providing data suitable for possible technological application of this natural material or similar synthetic ones. To pursue this goal, quantum mechanical simulations at the Density Functional Theory (DFT) level were employed, using the hybrid B3LYP functional, corrected to include the contribution of dispersive (van der Waals) forces, and all-electron Gaussian-type orbitals for each atom in the structure. A nature-based approach was followed to characterize the mineral phase, considering the Al substitutions on the composite bulk structure, to better compare the results with natural systems. The realized models were investigated both by hydrostatic compression, to calculate the equation of state, and axial deformations, to obtain the second-order elastic constants.

On second instance, the approach here presented for clinochlore can be applied to other nanostructured, heterodesmic layered materials, both natural and synthetic, and could be helpful to investigate and tailor the mechanical properties of this kind of materials.

2. Quantum mechanical approach

The simulations were performed using the CRYSTAL14 periodic code [22]. In the Density Functional Theory framework, the hybrid Becke, three-parameter [23], in combination with the gradient-corrected correlation functional of Lee, Yang, and Parr [24] was employed (B3LYP). The semi-empirical correction suggested by Grimme [25] and modified according to the B3LYP-D* scheme [26], has been adopted to take into account the dispersive forces contribution, as previously done for other minerals [11,16,27–32]. The Hamiltonian matrix has been diagonalized through the Monkhorst and Pack [33] scheme, using a 4 × 4 × 4 k-mesh, which leads to 36 reciprocal lattice points (k-points). This sampling grid allows a good sampling along the c-axis direction, which is important due to the dispersive forces acting in that direction.

Lattice constants and internal coordinates have been optimized within the same run using the analytical gradient method for the atomic positions and a numerical gradient for the unit-cell parameters. The Hessian matrix is upgraded with the Broyden–Fletcher–Goldfarb–Shanno algorithm [34–38]. The tolerances for the maximum allowed gradient and the maximum atomic displacement for considering the geometry as converged have been set to $6\cdot10^{-5}$ hartree bohr^{-1} and $1.2\cdot10^{-5}$ bohr, respectively.

Multi-electron wave functions are described by linear combination of crystalline orbitals (CO), expanded in terms of Gaussian-type orbital (GTO) basis sets. For all the calculations, oxygen has been described by a 8-411d11G basis sets, silicon by a 88-31G* and hydrogen by a 3-1p1G basis set. Aluminum and potassium atoms are described by a 8-511d1G and a 86-511G basis sets, respectively. The chosen basis sets are well balanced and, especially the one of the hydrogen atom, allows accurate calculations in both molecular and crystal structures with sustainable computational costs. Furthermore, they have been employed with good results in previous investigations on other silicates [11,16,27–32,39] and hydroxylapatite [32,40–46].

Graphical representations have been carried out with the molecular graphics program VESTA [47].

3. Results and discussion

3.1. Hydrostatic compression

The stoichiometric and Al-bearing clinochlore structures employed in the present work were already obtained in a recent work [16]. The composite has been modelled considering the experimental composition found in the cited work, namely two Al^{3+}/Mg^{2+} substitutions in the brucite-like layer and two Al^{3+}/Si^{4+} substitutions in the talc-like layer per unit cell were included, resulting in a bulk composition $[(Mg_2Al)^{VI}Mg_3{}^{VI}(Si_3Al)^{IV}O_{10}(OH)_8]$, with roman numbers indicating the coordination. For the sake of clearness, we report in Table 1 the geometrically optimized bulk models, both stoichiometric and Al-bearing, alongside the experimental XRD data.

The lattice parameters are in good agreement with those obtained from powder XRD refinement, in particular for the Al-bearing model, because its crystal-chemistry with one Al atom per two Mg in the brucite-like layer and one Al per three Si in the talc-like layer is very close to the experimental one. The **c**-axis length, which is the most influenced by van der Waals forces, almost match the experimental one. Thus, the semiempirical DFT-D2 scheme adequately provides a description of dispersive forces. It is worth noting that the presence of aluminium substitutions reduces the *c* lattice parameter value if compared to the pure chlorite model, due to the contribution of electrostatic forces between the brucite-like layer and the talc-like layer. The general small contraction of the theoretical lattice results for the Al-bearing clinochlore is mainly related to the absence of both temperature in the quantum mechanical simulations, *i.e.* the structural optimization took place at 0 K, and other ionic substitutions not contemplated in our models.

To simulate the compressional behaviour of clinochlore within the