Data Article

Dataset on the crystallographic, vibrational, and electronic properties of 1*M*-phlogopite K(Mg,Fe)$_3$(Si$_3$Al)O$_{10}$(OH)$_2$ obtained from Density Functional Theory investigations

Gianfranco Ulian, Giovanni Valdrè*

Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Centro di Ricerche Interdisciplinari di Biomineralogia, Cristallografia e Biomateriali, Università di Bologna "Alma Mater Studiorum" Piazza di Porta San Donato 1, 40126 Bologna, Italy

A R T I C L E I N F O

A B S T R A C T

The present work reports a dataset on the crystal structure, optical properties (complex dielectric function and refractive index), infrared, reflectance and Raman spectra, and electronic properties (band structure and density of states) of the 1*M*-polytype of phlogopite [1]. This phyllosilicate presents chemical formula K(Mg,Fe)$_3$(Si$_3$Al)O$_{10}$(OH)$_2$, with Mg/Fe ratio $\geq$ 2. The dataset was obtained from Density Functional Theory (DFT) simulations at B3LYP-D* level, i.e., with the hybrid functional B3LYP corrected with an *ad hoc* DFT-D2 scheme, and all-electron Gaussian-type orbitals basis sets for all atoms in the unit cell. Furthermore, experimental confocal Raman micro-spectrometry data (spectra) collected on a single crystal phlogopite specimen are reported. The quality of the dataset was assessed by comparing the results with available X-ray diffraction and IR/Raman spectroscopy data reported in literature. The reported complete dataset is a reference for future studies in fundamental georesource explo-

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

ration and exploitation, applied mineralogy, geology, and material science.

Specifications Table

Subject	Materials Science
Specific subject area	Mineralogy of phyllosilicates
Data format	Raw, Analyzed, Filtered
Type of data	Table, Graph
Data collection	Quantum mechanical simulations at the DFT/B3LYP-D* level of theory with the CRYSTAL17 code.
	Confocal Raman micro-spectrometry with 532 nm laser excitation source and nominal laser power of 30 mW. The spectra were processed with the WITec FIVE Plus software suite.
Data source location	University of Bologna, Dept. Biological, Geological and Environmental Sciences
Data accessibility	Repository name: Crystal-chemical, vibrational and electronic data of 1M-phlogopite [2]
	Data identification number: 10.17632/7wsntzztxw.1
	Direct URL to data: https://data.mendeley.com/datasets/7wsntzztxw/1
Related research article	G. Ulian, G. Valdrè, Crystal-chemical, vibrational and electronic properties of 1M-phlogopite $K(Mg,Fe)_3Si_3AlO_{10}(OH)_2$ from Density Functional Theory simulations, Applied Clay Science https://doi.org/10.1016/j.clay.2023.107166 (2023).

1. Value of the Data

- This extensive dataset features important properties of monoclinic 1M-phlogopite as a function of the iron content in the unit cell, representing a foundation for future fundamental and applied studies on this mineral and related phases.
- Raman and infrared spectroscopies are key investigation techniques to characterize georesources, in particular clay minerals.
- The calculated optical properties of 1M-phlogopite, i.e., complex dielectric function and refractive index, could be employed to develop materials with desired optical properties.
- The band structure and density of states could help to identify the effects of specific Fe^{2+}/Mg^{2+} substitutions on the electronic properties that, considering also the previous point, could be tailored for relevant optoelectronic applications.
- The present dataset could be used for direct comparison with other experimental and/or theoretical studies.

2. Data Description

The present dataset [2] was collected for 1M-phlogopite (commonly abbreviated Phl) $K(Mg,Fe)_3Si_3AlO_{10}(OH)_2$ using both theoretical methods and experimental measurements. In the repository, the data are subdivided into folders according to the following scheme (in parentheses, a brief description of the content is provided):

- DFT (main folder of the theoretical data)
  - Bands (electronic properties)
  - CIFs (structural data)
  - Figures (additional figures)
  - Tables (data collected into tables)

- Experimental
  - Raman spectra (confocal Raman micro-spectrometry data)

The theoretical data were collected for three specific 1*M*-phlogopite models, i.e., Phl-Fe0, Phl-Fe1 and Phl-Fe2 presenting chemical formulas $KMg_3Si_3AlO_{10}(OH)_2$, $KMg_{2.5}Fe_{0.5}Si_3AlO_{10}(OH)_2$, and $KMg_2FeSi_3AlO_{10}(OH)_2$, respectively. The name of the model indicates the number of iron atoms substituting magnesium ones in the unit cell.

The "Bands" folder contains several files with the calculated band structure and the density of states (DOSS) of each model. The DOSS are related to each specific atom in the mineral, i.e., potassium (K), magnesium (Mg), aluminum (Al), silicon (Si), iron (Fe), hydrogen (H), and apical (Oa), basal (Ob) and hydroxyl (Oh) oxygen atoms. The DOSS are projected on the electronic shells of each atom (*s, p, d*), and the total density of states is reported in the last column of each file.

The "CIFs" folder contains three Crystallographic Interchange Format files related to the Phl-Fe0, Phl-Fe1 and Phl-Fe2 1*M*-phlogopite models, geometrically optimized within the Density Functional Theory (DFT) approach.

"Figures" is a folder with a single image (FigS1.tif) associated with plots of the Raman intensity of the different as a function of the polarization direction of the incident radiation.

The "Tables" folder has five spreadsheets in Excel format containing the detailed atomic bond distances (Table_S1.xlsx), atomic dynamic charges (Table_S2.xlsx), complex dielectric function (Table_S3.xlsx) and refractive index (Table_S4.xlsx), IR absorption and reflectance spectra data (Table_S5.xlsx), and Raman intensities (Table_S6.xlsx).

Finally, the "Experimental > Raman spectra" folder contains eight ASCII files, each one reporting a single spectrum measured with confocal Raman micro-spectrometry on a single-crystal specimen of 1*M*-phlogopite. The spectra are repeated measurements collected from different positions of the same phlogopite sample. The experimental spectrum shown in Fig.S1 is the one reported in the "Phlogopite-1M–Spectrum–007.txt" file.

3. Experimental Design, Materials and Methods

3.1. Theoretical Methods

Density Functional Theory simulations with the CRYSTAL17 code were employed to obtain the present dataset [3]. In this framework, the well-known hybrid B3LYP functional [4,5] was adopted in the calculations because of its high accuracy when describing the structural, electronic and vibrational properties of crystalline and molecular materials [6–8]. At the same time, this functional was corrected with an *ad hoc* DFT-D2 scheme to properly treat long-range interactions, leading to the so-called B3LYP-D* approach [9].

The Kohn-Sham orbitals were built using a linear combination of atomic orbitals (LCAO), which in turn were described as Gaussian-type orbitals (GTO). Specifically, the atomic basis sets were 86–511 G for K, 88–31G* for silicon, 85–11G* for aluminum, 8–511d1G for magnesium, 86–411d41G for iron, 8–411d11G for oxygen, and 3–1p1G for hydrogen. were 88–31G*,85–11G*, 8–511d1G, 8–411d11G and 3–1p1G, respectively [10–12].

The exchange and correlation contributions to the total energy were calculated on a pruned grid of 75 points and 974 angular points (XLGRID keyword in CRYSTAL17), obtained according to the Gauss–Legendre quadrature and Lebedev schemes. The tolerance thresholds that control accuracy of the Coulomb and exchange integrals were set to 10^{-8} (TOLINTEG keyword, ITOL1 to ITOL4) and 10^{-16} (ITOL5), respectively [3]. The Hamiltonian matrix was diagonalized with a $5 \times 5 \times 5$ Monkhorst-Pack grid of 39 *k*-points in the first Brillouin zone. The convergence on the total energy (TOLDEE keyword) was reached when the difference between the energy of two subsequent self-consistent field cycles was less than 10^{-8} Hartree for all calculations but the evaluation of the phonon properties, for which a tighter tolerance was set (10^{-10} Hartree) because of they are obtained from numerical differentiation (dynamic matrix / forces calculation) [10].

Harmonic phonon modes were calculated at the Γ point on the optimized models of monoclinic 1M-phlogopite by diagonalizing the mass-weighted Hessian matrix (dynamical matrix), whose elements are the second derivatives of the lattice potential to mass-weighted atomic displacements [13].

Infrared and Raman intensities were calculated analytically. The IR absorbance spectrum $A(\nu)$ of clinochlore was calculated using different adsorption formulas [14], starting from the complex dielectric function $\varepsilon(\nu)$ obtained from the Drude-Lorentz model for each inequivalent polarization direction:

$$\varepsilon_{ii}(\nu) = \varepsilon_{\infty,ii} + \sum_p \frac{f_{p,ii}\nu_p^2}{\nu_p^2 - \nu^2 - i\nu\gamma_p} \tag{1}$$

where ii is the polarization direction, ε_∞ is the optical dielectric tensor, ν_p, f_p and γ_p are the (transverse optical) vibrational frequency, the oscillator strength and the damping factor for the pth phonon mode. Both real $Re[\varepsilon(\nu)]$ and imaginary $Im[\varepsilon(\nu)]$ parts of the dielectric function were calculated.

The complex refractive index, $\bar{n} = n + ik$, with n the phase velocity and k the extinction coefficient are calculated as:

$$\begin{aligned} n_{ii}^2(\nu) - k_{ii}^2(\nu) &= Re[\varepsilon_{ii}(\nu)] \\ 2n_{ii}(\nu)k_{ii}(\nu) &= Im[\varepsilon_{ii}(\nu)] \end{aligned} \tag{2}$$

The reflectance spectrum, $R_{ii}(\nu)$, is computed for each inequivalent direction ii as:

$$R_{ii}(\nu) = \left| \frac{\sqrt{\varepsilon_{ii}(\nu) - \sin^2(\theta)} - \cos(\theta)}{\sqrt{\varepsilon_{ii}(\nu) - \sin^2(\theta)} + \cos(\theta)} \right|^2 \tag{3}$$

with θ the incidence angle of the beam to the normal of the crystal surface. For the calculations related to the present dataset, this angle was set to $0°$.

Then, the infrared absorbance was calculated with four different models, the first being the only one that does not need the complex dielectric function. In this case, the IR absorbance was obtained by raw superposition of Lorentzian peaks according to the formula:

$$A_{Lorentzian}(\nu) = \sum_p \frac{I_p}{\pi} \frac{\gamma_p/2}{(\nu - \nu_p)^2 - \gamma_p^2/4} \tag{4}$$

The second model is a classical absorption formula, averaged over the polarization direction xx, yy and zz (1, 2 and 3, according to the Voigt's notation):

$$A_{classical}(\nu) = \frac{1}{3} \sum_{ii=1}^{3} \frac{4\pi}{\lambda\rho} k_{ii}(\nu) \tag{5}$$

with λ the wavelength of the incident beam and ρ the mineral density. The last two formulas involve Rayleigh approximation of particles either having spherical shape (third formulation) and as continuous distribution of ellipsoids (fourth formula):

$$A_{spherical}(\nu) = \frac{1}{3} \sum_{ii=1}^{3} \frac{2\pi}{\lambda\rho} Im\left[\frac{\varepsilon_{ii}(\nu) - 1}{\varepsilon_{ii}(\nu) + 2} \right] \tag{6}$$

$$A_{ellipsoidal}(\nu) = \frac{1}{3} \sum_{ii=1}^{3} \frac{2\pi}{\lambda\rho} Im\left[\frac{2\varepsilon_{ii}(\nu)}{\varepsilon_{ii}(\nu) - 1} \log \varepsilon_{ii}(\nu) \right] \tag{7}$$

The Raman spectra were calculated by considering the mineral both as a polycrystalline powder and as a single-crystal. Their construction is based on the transverse optical vibrational

modes of phlogopite through a pseudo-Voigt functional form [15,16]:

$$A(\nu) = \eta L(\nu) + (1 - \eta)G(\nu) \tag{8}$$

In Eq. (8), $A(\nu)$ is the Raman intensity, $L(\nu)$ is a Lorentzian function with formula given by Eq. (4), η is the Lorentzian factor and $G(\nu)$ is a Gaussian function given by:

$$G(\nu) = \sum_p 2\sqrt{\frac{\ln 2}{\pi}}\frac{I_p}{\gamma_p}exp\left[-\frac{4\ln 2(\nu - \nu_p)^2}{\gamma_p^2}\right] \tag{9}$$

with I_p the computed Raman intensities for the pth vibrational mode.

All of the above optical and vibrational quantities were calculated in the spectral range 0–4000 cm^{-1}. The optical dielectric tensor, ε_∞, was computed using a couple-perturbed Kohn-Sham approach [17,18]. The damping factor represents the full width at half maximum of each vibrational mode and was set to 8 for both infrared and Raman spectra because this value provides band broadening similar to that of experimental samples and is also the default employed by CRYSTAL, as described by Maschio and co-workers [14]. Raman spectra were simulated using a pure Lorentzian form, which is the default of CRYSTAL17 [15], corresponding to $\eta = 1$, to obtain the typical sharp peaks of Raman spectra [19]. Also, the Raman intensities were calculated considering a 532 nm laser source at 298 K, conditions matching the experimental measurements that were here used (see below).

3.2. Experimental Methods

The dataset of experimental Raman spectra of 1M-phlogopite was collected from a single-crystal sample BU1–7, which was taken from the BU1 rock from the deposits of the Bunyampaka maar (Kasenyi field). This sample was characterized in previous work using electron probe microanalysis, Mössbauer spectroscopy and single-crystal X-ray diffraction [20]. The calculated chemical formula of this mineral is $(K_{0.90}Na_{0.05}Ba_{0.01})$ $[Mg_{2.34}Al_{0.08}Fe(II)_{0.20}Fe(III)_{0.08}Ti_{0.26}Cr_{0.05}]$ $[Si_{2.87}Al_{1.07}Fe(III)_{0.06}]$ $O_{10.58}(F_{0.10}OH_{1.31})$, with two unit formulas ($Z = 2$) in the monoclinic (space group $C2/m$) crystallographic cell of lattice parameters $a = 5.3259(2)$ Å, $b = 9.2245(3)$ Å, $c = 19.2309(4)$ Å and $\beta = 100.050(2)°$.

Several Raman spectra were collected at room temperature ($\sim$20 °C) using a WITec Alpha 300R confocal Raman microscopy system, made of an optical microscope and an ultra-high throughput UHTS 300 VIS spectrometer with CCD camera and gratings of 600 g/mm. A green laser beam (532 nm) was used as excitation light, setting a power of 30 mW to prevent heating the sample and possible alterations on the mineral. The laser beam was focused on the sample with a 100$\times$ Zeiss microscope objective with a low numerical aperture objective (NA = 0.50) to avoid optical artefacts. The backscattered Raman spectra were collected in confocal mode between 100 and 4000 cm^{-1}, with a resolution of about 2.7 cm^{-1} and an acquisition time of 10 min. The Rayleigh scattering line was removed by an edge filter.

The spectra were processed using the WITec Project FIVE software to remove the cosmic rays and subtract the background. The first operation involved a cosmic ray detection algorithm with filter size and dynamic factor set to 4 and 4.4, respectively. The background was subtracted with a rolling-ball algorithm (called "shape" in the software), using a rounded shape with a size of 100 pixels. The experimental Raman data were then exported, with a spectral range from ca. 35 cm^{-1} to about 4180 cm^{-1}.

Limitations

Not applicable.

Ethics Statement

The authors have read and follow the ethical requirements for publication in Data in Brief. The present work does not involve human subjects, animal experiments, or any data collected from social media platforms.

Data Availability

https://data.mendeley.com/datasets/7wsntzztxw/1 (Original data) (Mendeley Data)

CRediT Author Statement

Gianfranco Ulian: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Visualization, Writing – original draft; **Giovanni Valdrè:** Conceptualization, Validation, Investigation, Resources, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

References

[1] G. Ulian, G. Valdrè, Crystal-chemical, vibrational and electronic properties of 1M-phlogopite K(Mg,Fe)$_3$Si$_3$AlO$_{10}$(OH)$_2$ from Density Functional Theory simulations, Appl. Clay Sci. (2023), doi:10.1016/j.clay.2023.107166.

[2] G. Ulian, G. Valdrè, Crystal-Chemical, Vibrational and Electronic Data of 1M-Phlogopite, 2023 Mendeley Data, V1, doi:10.17632/7wsntzztxw.1.

[3] R. Dovesi, V.R. Saunders, C. Roetti, R. Orlando, C.M. Zicovich-Wilson, F. Pascale, B. Civalleri, K. Doll, N.M. Harrison, I.J. Bush, P. D'Arco, M. Llunell, M. Causà, Y. Noel, L. Maschio, A. Erba, M. Rerat, S. Casassa, CRYSTAL17 User's Manual, University of Torino, Torino, 2017.

[4] A.D. Becke, Density-functional thermochemistry .3. The role of exact exchange, J. Chem. Phys. 98 (7) (1993) 5648–5652, doi:10.1063/1.464913.

[5] C.T. Lee, W.T. Yang, R.G. Parr, Development of the colle-salvetti correlation-energy formula into a functional of the electron-density, Phys. Rev. B 37 (2) (1988) 785–789, doi:10.1103/PhysRevB.37.785.

[6] G. Ulian, G. Valdrè, Effects of fluorine content on the elastic behavior of topaz Al$_2$SiO$_4$(F,OH)(2), Am. Mineral. 102 (1–2) (2017) 347–356, doi:10.2138/am-2017-5668.

[7] G. Ulian, D. Moro, G. Valdrè, First principle investigation of the mechanical properties of natural layered nanocomposite: clinochlore as a model system for heterodesmic structures, Compos. Struct. 202 (2018) 551–558, doi:10.1016/j.compstruct.2018.02.089.

[8] G. Ulian, G. Valdrè, Structural, vibrational and thermophysical properties of pyrophyllite by semi-empirical density functional modelling, Phys. Chem. Miner. 42 (7) (2015) 609–627, doi:10.1007/s00269-015-0748-7.

[9] B. Civalleri, C.M. Zicovich-Wilson, L. Valenzano, P. Ugliengo, B3LYP augmented with an empirical dispersion term (B3LYP-D*) as applied to molecular crystals, CrystEngComm 10 (4) (2008) 405–410, doi:10.1039/b715018k.

[10] M. Catti, G. Valerio, R. Dovesi, Theoretical study of electronic, magnetic, and structural properties of α-Fe2O3 (hematite), Phys. Rev. B 51(12) (1995) 7441–7450. https://doi.org/10.1103/PhysRevB.51.7441.

[11] G. Ulian, D. Moro, G. Valdrè, Infrared and Raman spectroscopic features of clinochlore Mg$_6$Si$_4$O$_{10}$(OH)$_8$: a density functional theory contribution, Appl. Clay Sci. 197 (2020) 105779, doi:10.1016/j.clay.2020.105779.

[12] G. Ulian, G. Valdrè, Density functional investigation of the thermo-physical and thermo-chemical properties of 2M(1) muscovite, Am. Mineral. 100 (4) (2015) 935–944, doi:10.2138/am-2015-5086.

[13] F. Pascale, C.M. Zicovich-Wilson, F.L. Gejo, B. Civalleri, R. Orlando, R. Dovesi, The calculation of the vibrational frequencies of crystalline compounds and its implementation in the CRYSTAL code, J. Comput. Chem. 25 (6) (2004) 888–897, doi:10.1002/Jcc.20019.

[14] L. Maschio, B. Kirtman, R. Orlando, M. Rerat, Ab initio analytical infrared intensities for periodic systems through a coupled perturbed Hartree-Fock/Kohn-Sham method, J. Chem. Phys. 137 (20) (2012) 204113, doi:10.1063/1.4767438.

[15] L. Maschio, B. Kirtman, M. Rerat, R. Orlando, R. Dovesi, Ab initio analytical Raman intensities for periodic systems through a coupled perturbed Hartree-Fock/Kohn-Sham method in an atomic orbital basis. I. Theory, J. Chem. Phys. 139 (16) (2013) 164101, doi:10.1063/1.4824442.

[16] L. Maschio, B. Kirtman, M. Rerat, R. Orlando, R. Dovesi, Ab initio analytical Raman intensities for periodic systems through a coupled perturbed Hartree-Fock/Kohn-Sham method in an atomic orbital basis. II. Validation and comparison with experiments, J. Chem. Phys. 139 (16) (2013) 164102, doi:10.1063/1.4824443.

[17] M. Ferrero, M. Rerat, B. Kirtman, R. Dovesi, Calculation of first and second static hyperpolarizabilities of one- to three-dimensional periodic compounds. Implementation in the CRYSTAL code, J. Chem. Phys. 129 (24) (2008) 244110, doi:10.1063/1.3043366.

[18] M. Ferrero, M. Rerat, R. Orlando, R. Dovesi, The calculation of static polarizabilities of 1-3D periodic compounds. The implementation in the CRYSTAL code, J. Comput. Chem. 29 (9) (2008) 1450–1459, doi:10.1002/jcc.20905.

[19] R. Dovesi, A. Erba, R. Orlando, C.M. Zicovich-Wilson, B. Civalleri, L. Maschio, M. Rerat, S. Casassa, J. Baima, S. Salustro, B. Kirtman, Quantum-mechanical condensed matter simulations with CRYSTAL, Wiley Interdiscip. Rev. 8 (4) (2018) E1360, doi:10.1002/Wcms.1360.

[20] M. Lacalamita, E. Mesto, F. Scordari, E. Schingaro, Chemical and structural study of 1M- and 2M (1)-phlogopites coexisting in the same Kasenyi kamafugitic rock (SW Uganda), Phys. Chem. Miner. 39 (8) (2012) 601–611, doi:10.1007/s00269-012-0515-y.