Exploring the structural and optoelectronic properties of natural insulating phlogopite in van der Waals heterostructures

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Abstract
Naturally occurring van der Waals crystals have brought unprecedented interest to nanomaterial researchers in recent years. So far, more than 1800 layered materials (LMs) have been identified but only a few insulating and naturally occurring LMs were deeply investigated. Phyllosilicate minerals, which are a class of natural and abundant LMs, have been recently considered as a low-cost source of insulating nanomaterials. Within this family an almost barely explored material emerges: phlogopite (KMg$_3$(AlSi$_3$)O$_{10}$(OH)$_2$). Here we carry out a high throughput characterization of this LM by employing several experimental techniques, corroborating the major findings with first-principles calculations. We show that monolayers (1L) and few-layers of this material are air and temperature stable, as well as easily obtained by the standard mechanical exfoliation technique, have an atomically flat surface, and lower bandgap than its bulk counterpart, an unusual trend in LMs. We also systematically study the basic properties of ultrathin phlogopite and demonstrate that natural phlogopite presents iron impurities in its crystal lattice, which decreases its bandgap from about 7 eV to 3.6 eV. Finally, we combine phlogopite crystals with 1L-WS$_2$ in ultrathin van der Waals heterostructures and present a photoluminescence study, revealing a significant enhancement on the 1L-WS$_2$ optical quality (i.e. higher recombination efficiency through neutral excitons) similarly to that obtained on 1L-WS$_2$/hexagonal boron nitride heterostructures. Our proof-of-concept study shows that phlogopite should be regarded as a good and promising candidate for LM-based applications as a low-cost layered nanomaterial.

1. Introduction
Layered materials (LMs) [1], for which graphene is the prime example, have obtained vast attention in the last years. So far, more than 1800 LMs have been computationally identified [2–4], while many of them have been naturally obtained or synthesized [5–13]. Thus, as soon as a new LM is identified, the investigation of its optical, mechanical and electrical properties is promptly examined [14]. Moreover, with the advent of techniques able to stack LMs precisely one on top of another creating the so-called van der Waals heterostructures (vdWHs) [15], new applications and studies are envisioned [16–18]. Consequently, individual LMs and their vdWHs are often considered...
as building blocks for future optoelectronic devices [14–17, 19, 20].

Despite the massive use of synthetic hexagonal boron nitride (hBN) as an insulator in vdWHs, the search for earth-abundant LMs sources that could potentially replace hBN is of great importance [21–23]. In this scenario, the mica group, which is one of the groups of sheet silicate (phyllosilicate) minerals and shows perfect basal cleavage [24, 25], has driven the interest of many research groups because of its thermal, mechanical and electrical performance [26–31], its easy assembly in vdWHs [32, 33], and its use as substrate in LMs growth [34, 35]. All these qualities have boosted its applications [36]. Nevertheless, most of the investigations have focused on muscovite mica, and barely exploited other minerals of this family, for instance, phlogopite. Phlogopite is a common phyllosilicate within the mica group with chemical formula KMg₃(AlSi₃)O₁₀(OH)₂ [37]. Some works have been done regarding its mechanical [38] and structural stability [39, 40], electrical [30, 31] and optical [41–44] properties in the bulk form, and its liquid phase [45] and mechanical [5, 28] exfoliation capability. However, to the best of our knowledge, no systematical study has been performed to investigate the basic properties of phlogopite in the ultrathin form and its use in vdWHs with other LMs. Here, we demonstrate that phlogopite is air-stable, can be mechanically exfoliated down to monolayers (1L), and has atomically flat surfaces like those obtained in hBN flakes. We present a robust experimental characterization of the phlogopite crystals by means of x-ray diffraction (XRD), x-ray fluorescence (XRF) mapping, wavelength-dispersive spectroscopy (WDS), electron paramagnetic resonance (EPR), optical absorption measurements (UV–vis–NIR), atomic force microscopy (AFM), Raman, Mössbauer and Fourier-transform infrared (FTIR) spectroscopies, in addition with first-principles calculations. We then describe the basic structural, electronic structure, and optical features of this crystal and demonstrate that natural phlogopite presents iron (Fe) impurities in different sites and valence states in its crystal lattice, which decrease its bandgap from about 7 eV to 3.6 eV mainly by the incorporation of Fe²⁺ in Mg²⁺ sites. We demonstrate that the thickness reduction also leads to a bandgap decrease, an unusual trend in LMs. Finally, we show that insulating phlogopite supports thermal and hydrogen annealing, and it can be easily embedded in vdWHs, increasing the photoluminescence (PL) quality of 1L-WS₂ (i.e. higher recombination efficiency through neutral excitons, X⁰) similarly to what is achieved in 1L-WS₂/hBN heterostructures. Therefore, we foresee the use of phlogopite layers in ultrathin electronics and flexible devices [46, 47], as well as in experiments dealing with nanophotonics [48, 49].

2. Results and discussion

We start by discussing the structural characterization of a natural phlogopite crystal. From the analysis, we obtain a complete structural description of the sample examined. Mineral phlogopite (inset in figure 1(a)), obtained from Minas Gerais (Brazilian mine at Itabira city), was used to produce the exfoliated samples investigated in this work. To confirm the structure and chemical composition of the bulk material, we initially investigated it by XRD (see section 4 for details). Figure 1(a) plots the XRD diffractogram retrieved from a powdered sample of the crystal using a conventional laboratory source and Cu K-alpha radiation (λ = 1.541 Å). The sharp and intense peaks clearly show the crystalline nature of the sample. Given the mineral origin of the sample, different phases of phyllosilicates were searched to provide possible fits with the presence of major and minor phases. After going through search algorithms, Rietveld refinement was carried out using the MAUD package [50]. The best fitting to the experimental data, matching peak intensities and positions is retrieved for a volumetric combination of 98% phlogopite [51] and 2% biotite [52]. The parameters retrieved for the dominant phlogopite phase are a = 5.338 Å, b = 9.229 Å, c = 10.284 Å, α = 90°, β = 99.993°, and γ = 90°. A fit of the peaks using only the phlogopite phase is shown in figure 1(a). The retrieved lattice values are consistent with those reported in the literature [53, 54], but the lattice parameters may vary with the increasing contents of cations with different ionic radii [55]. The mineral exhibits a lamellar structure oriented along the (001) direction. The pristine crystal displays monoclinic lattice, with symmetries from the space group P2₁/m (C2/m), where two tetrahedral silicate sheets are adjacent to one octahedral layer—TOT structure, also known as 2:1 layered silicate structure [24, 25, 56], and its crystallographic representation is given in figure 1(b). Pristine phlogopite (‘colorless’, Fe-free crystal) is a hydrated phyllosilicate of potassium (K) and magnesium (Mg) with chemical formula KMg₃AlSi₃O₁₀(OH)₂, while the Fe-endmember (‘brown’ mineral) is the annite mineral (KFe₂AlSi₃O₁₀(OH)₂), and the biotite mineral can be seen as a Fe-rich crystal with chemical formula (K(Mg,Fe₃)AlSi₃O₁₀(OH)₂) [24, 25, 56]. However, in natural materials the existence of impurities such as Fe ions in their crystal lattice is reported in [13, 57–59]. Consequently, it is common to observe Fephlogopite crystals (light and dark brown minerals) with different Fe ions concentrations [37, 41, 59].

Next, the chemical composition of the phlogopite sample is determined by WDS, XRF mapping, EPR, and UV–vis (see section 4 for details regarding the measurements). Quantitative analysis by WDS provide a content of 41.9(8)% of SiO₂, 24.7(6)% of MgO, 15.6(3)% of Al₂O₃, 6.9(1)% of...
K$_2$O, 5.0(1)% of FeO and a content about 1% of other trace impurities, while the remaining contribution is due to the presence of water in the mineral structure. The WDS chemical evaluation indicates different impurities in natural phlogopite, with Fe being the predominant impurity. In accordance with this data, the XRF emission and mapping demonstrate qualitatively that Fe ions are largely predominant (figure S1 available online at stacks.iop.org/2D_Mater/9/035007/mmedia) and homogeneously distributed in the analyzed area as shown in figure 2(a), respectively. In the supplementary information, the Raman and FTIR analyses of our phlogopite sample also suggest the existence of impurities. Fe impurities are frequently present in the phlogopite structure as substitutional ions to Al$^{3+}$ or Mg$^{2+}$, being able to occupy both tetrahedral and octahedral sites [60]. The Fe ions can be present in the phlogopite structure with different valence states, Fe$^{2+}$ and Fe$^{3+}$. However, Fe$^{2+}$ ions with 3d electronic configuration are non-Kramer ions, being generally unobservable by EPR [61, 62]. For the Fe$^{3+}$ (3d$^5$) ions with an effective electronic spin $S = 5/2$, at least four orthorhombic sites have already been identified by the EPR technique [60, 63, 64], being two tetrahedral and two (most commonly reported) octahedral sites. One octahedral site is determined by the Fe ion surrounded by four oxygen (O) ions and two hydroxyl (OH) ions at opposite vertices (Oc$^1$), while the other octahedral site (Oc$^2$) is characterized by OH ions occupying adjacent vertices [60, 64]. The Fe$^{3+}$ ions experience a strong orthorhombic crystalline electric field that is sufficient to raise the degeneracy of Kramer’s doublets with the environment symmetry varying from axial to rhombic [60]. As a result of the strong crystalline field, the octahedral substitutional sites for the Fe impurities must be distorted [60, 63, 64]. The octahedral site (Oc$^2$) with adjacent OH ions is the most rhombic one, resulting in an isotropic EPR line at $g \sim 4.2$ in phlogopite samples [60, 63, 64], while the octahedral site (Oc$^1$) with OH ions at the opposite vertices presents symmetry with nearly axial character [60]. EPR measurements at 75 K performed rotating the phlogopite sample with the c axis perpendicular to the rotation axis (figure 2(b)) reveal an approximately isotropic line at $g \sim 4.2$ that are characteristic to the most rhombic octahedral site (Oc$^2$) for substitutional Fe ions in phlogopite. Some broad anisotropic lines at lower magnetic fields are also observed, possibly due to the substitutional Fe$^{3+}$ ions in the Oc$^1$ site. However, due to the widening of the EPR lines, it is not possible to conclude about the presence or not of substitutional Fe$^{3+}$ impurities also in tetrahedral sites from our EPR spectra. For the angular dependence of EPR spectra with the rotation axis parallel to the c axis (figure S2), only a broad unresolved isotropic signal around $g \sim 4.2$ is observed. Our EPR measurements agree with previous works [44, 60, 63, 64] and suggest that substitutional Fe$^{3+}$ ions are present in the phlogopite sample at least in one octahedral sites distorted by strong rhombic crystalline field. The broadening of the anisotropic lines in lower magnetic fields could be associated to the exchange interaction between the Fe impurities or due to the superposed slightly different orientations of the paramagnetic centers contributing to EPR spectra due to non-aligned stacking regions of the phlogopite lamellar structure.

Since EPR measurements are not sensitive to Fe$^{2+}$ ions, UV–vis–NIR absorption measurements and Mössbauer spectroscopy are then performed (see section 4 for details regarding the measurements). The absorbance spectrum of our phlogopite sample (figure 2(c)) reveals bands associated with Fe impurities in both Fe$^{2+}$ and Fe$^{3+}$ valence states. The various absorption bands observed below 600 nm are due to orbital electronic transitions of...
Figure 2. Experimental characterization of Fe:phlogopite sample. (a) XRF mapping for Fe impurities over a 250 × 250 µm² region and over an isolated Fe island (inset, 5 × 5 µm², scale bar 1 µm) on phlogopite crystal. The images are obtained from the selection of Fe K alpha emission line, excited under 7.2 keV, and normalized by the intensity of the hottest pixel of each image. Red (blue) indicates a higher (lower) Fe concentration. (b) The angular dependence of phlogopite EPR spectra at 75 K with 9.440(1) GHz performed with the c axis perpendicular to the rotation axis indicate a typical dependence of Fe³⁺ ions in distorted octahedral sites. (c) The absorbance spectrum of a phlogopite flake confirms the presence of Fe impurities in different valence states. The Tauc plot (inset) based on the reflectance measurement of a phlogopite flake indicates an experimental direct optical bandgap of about 3.6 eV determined by the Kubelka–Munk method. (d) Fitted (red line) Mössbauer phlogopite spectrum indicating the presence of Fe²⁺ (blue line) at octahedral sites and Fe³⁺ at octahedral (continuous green line) and tetrahedral (dashed green line) sites with contributions of 53.7% and 46.3%, respectively.

Fe³⁺ ions, while the two broad bands at approximately 900 nm and 1100 nm are due to the presence of Fe²⁺ ions also in octahedral sites [65, 66]. The absorption band observed around 700 nm is due to the charge transfer between the Fe ions [65, 66]. Now, in order to determine the experimental optical bandgap of our phlogopite sample, a Tauc plot is elaborated from reflectance measurements of a phlogopite flake (inset in figure 2(c)). The bandgap is obtained by extrapolation of the linear behavior (red dashed line) of the Kubelka–Munk function of the data [67, 68]. Considering a direct bandgap for phlogopite minerals [44], we estimate an experimental bandgap of about 3.6 eV for our sample that is in agreement with previous work on natural phlogopite [69], and lower than that in synthetic phlogopite [70] of 7.8 eV. The fitted phlogopite Mössbauer spectrum is shown in figure 2(d). The spectrum is fitted (red line) with three contributions of Fe doublets: the blue line component is assigned to (VI)Fe²⁺ doublet and it corresponds to bivalent Fe impurities in octahedral sites (six-coordination), while the green lines components are assigned to (VI)Fe³⁺ (continuous line) and (IV)Fe³⁺ (dashed line) doublets, corresponding respectively to trivalent Fe impurities in octahedral and tetrahedral sites (four-coordination). The retrieved hyperfine parameters from the fit are 1.11, 0.39 and 0.16 mm s⁻¹ for the isomeric shift and 2.52, 1.08 and 0.37 mm s⁻¹ for the quadrupole splitting for the (VI)Fe²⁺, (VI)Fe³⁺ and (IV)Fe³⁺ doublets, respectively. Quantifying the relative contribution of Fe ions from the absorption areas, we obtain a contribution of 53.7% due to Fe²⁺ ions and 46.3% to Fe³⁺ ions (22.0% in octahedral sites and 24.3% in tetrahedral sites). Thus, we can conclude that the incorporation of Fe impurities in the phlogopite structure occurs preferentially in the bivalent state at octahedral sites, while the Fe³⁺ ions are present as substitutional impurities in both octahedral and tetrahedral sites, assuming different coordinations for the trivalent Fe ions in agreement with the literature [65, 71, 72]. This result complements our previous analysis by XRF, EPR and absorption measurements, giving a complete experimental description of the Fe incorporation in the phlogopite mineral.

The presence of impurities in micas were pointed as a possible reason for the lower bandgap of natural micas in comparison to that of synthetic micas [44, 70]. In order to understand the influence of Fe impurities on the electronic structure of phlogopite, we perform density functional theory
Figure 3. Atomistic model of the analyzed Fephlogopite structures. (a) Pristine phlogopite (Mg$_6$(AlSi$_3$)O$_{20}$(OH)$_4$K$_2$). Phlogopite (Mg$_6$Fe$_2$(AlSi$_3$)O$_{20}$(OH)$_4$K$_2$) with Fe$^{2+}$ ions at the (b) Oc$^1$ and (c) Oc$^2$ sites, respectively. (d) Phlogopite (Mg$_6$(AlFeSi$_3$)O$_{20}$(OH)$_4$K$_2$) with Fe$^{3+}$ ions at the tetrahedral (tt) site. Phlogopite (Mg$_6$Fe$_2$(AlSi$_3$)O$_{20}$(OH)$_4$K$_2$) with Fe$^{2+}$ ions at the (e) Oc$^1$ and (f) Oc$^2$ sites, respectively.

(DFT) calculations (see section 4 for more details), considering the five most likely substitutional sites for Fe ions. These sites are based on our experimental results, previous literature [65, 71, 72], and the Hume–Rothery rule [73]. Figure 3(a) shows the supercell atomistic model for the pristine phlogopite (Mg$_6$(Al$_2$Si$_3$)O$_{20}$(OH)$_4$K$_2$). Figures 3(b) and (c) illustrates the isovalent substitutions of Mg$^{2+}$ by Fe$^{2+}$, where a single Fe$^{2+}$ ion occupies the two inequivalent octahedral sites Oc$^1$ and Oc$^2$, respectively. The substitution of (VI)Fe$^{2+}$ at the (VI)Mg$^{2+}$ site results in a difference of effective ionic radii, $\delta r$, of approximately 8%. Figure 3(d) shows the case for an isovalent substitution of Al$^{3+}$ by Fe$^{2+}$ ion, occupying the tetrahedral site of Al, named as tt site. Although the substitution of (IV) Al$^{3+}$ by (IV) Fe$^{2+}$ violates the Hume–Rothery rule ($\delta r \sim 25\%$), it occurs in nature [65, 71, 72]. Other cases for Fe$^{2+}$ or Fe$^{3+}$ ions in the tetrahedral layer, as (IV)Fe$^{2+}$ at the (IV)Al$^{3+}$ site ($\delta r \sim 62\%$), (IV)Fe$^{3+}$ at the (IV)Si$^{4+}$ site ($\delta r \sim 142\%$), (IV)Fe$^{3+}$ at the (IV)Si$^{4+}$ site ($\delta r \sim 89\%$) were neglected, due to the large $\delta r$, and lack of experimental evidence in our data. Figures 3(e) and (f) shows the case of substitution of Mg$^{2+}$ by Fe$^{2+}$ ions in the Oc$^1$ and Oc$^2$, respectively. These are no isovalent substitutions, and we consider the additional substitution of Si$^{4+}$ by Al$^{3+}$ ion for charge compensation, since its substitution is naturally present in the phlogopite structure.

The calculated lattice parameters of pristine phlogopite, by using local-density approximation (LDA) for the exchange-correlation functional, are $a = 5.169$ Å, $b = 8.958$ Å, $c = 9.842$ Å, $\alpha = 90^\circ$, $\beta = 100.6^\circ$, and $\gamma = 90^\circ$, in close agreement to our experimental findings. Table 1 summarizes the structural changes of phlogopite induced by the different Fe ions analyzed. The presence of Fe ions increases the lattice parameters and cell volume $V$(cell), regardless the occupation site. The volume of the octahedral sites $V$(Oc$^1$) and $V$(Oc$^2$) are essentially equal in the pristine material. In the phlogopite with Fe$^{2+}$ ions, the volume of the octahedron site with the Fe$^{2+}$ ion is greater than that with Mg$^{2+}$. In more detail, for the Oc$^1$Fe$^{2+}$ geometry, the Fe$^{2+}$ ion occupies the Oc$^1$ site, with a volume $V$(Oc$^1$) of about 11% larger than that of the Oc$^2$ site, which host the Mg$^{2+}$ ion. A similar trend is obtained for the relative volumes of the $V$(Oc$^1$) and $V$(Oc$^2$) site in the Oc$^2$:Fe$^{2+}$ geometry, where Fe$^{2+}$ and Mg$^{2+}$ ions exchange places in comparison to the Oc$^1$:Fe$^{2+}$ geometry. In the case of Fe$^{3+}$ ions in the octahedra site, the volume of the octahedron hosting the Fe$^{3+}$ is around 0.7% smaller than that of the octahedron hosting the Mg$^{2+}$. The lattice expansion is attributed to the increase of the volume of the tetrahedron $T_{Si}$, which hosts the Al$^{3+}$ ion, added for charge compensation in place of Si. The volume of $T_{Si}$, $V(T_{Si})$, increases of 21% in comparison to the $V(T_{Si})$ in the pristine geometry, when $T_{Si}$ hosts the Si$^{3+}$ ion. When the Fe$^{3+}$ impurity is at the tetrahedron site tt, the volumes of the octahedra sites Oc$^1$ and Oc$^2$ differ in about 0.5%, and the volume expansion is attributed to the increase in the volume of the tetrahedron tt, $V$(tt), by about 30%. These results agree with the expected effective ionic radii differences of the ions [74]. These impurity-induced geometry modifications are expected to impact the
Table 1. Structural parameters of phlogopite crystals, as calculated by using LDA exchange-correlation functional. The lattice constants, $a$, $b$, $c$; volumes of the supercell, $V(\text{cell})$; volumes of the octahedral site $V(\text{Oc})$, $V(\text{Oc}^2)$, where the substitution of $\text{Mg}^{2+}$ by $\text{Fe}^{2+}$ or $\text{Fe}^{3+}$ ions were considered; volume of the tetrahedral site $V(\text{T}_{1\text{L}})$, where the substitution of $\text{Si}^{4+}$ by $\text{Al}^{3+}$ ion, and volume of the tt site, $V(\text{tt})$, where the substitution of $\text{Al}^{3+}$ by $\text{Fe}^{3+}$ ion were considered, are in angstrom. The angles between the lattice constants, $\alpha$, $\beta$, and $\gamma$ are in degrees.

|          | $a$   | $b$   | $c$   | $\alpha$ | $\beta$ | $\gamma$ | $V(\text{cell})$ | $V(\text{Oc})$ | $V(\text{Oc}^2)$ | $V(\text{T}_{1\text{L}})$ | $V(\text{tt})$ |
|----------|-------|-------|-------|----------|---------|-----------|------------------|----------------|------------------|---------------------|--------------|
| Pristine | 5.169 | 8.958 | 9.843 | 90.00    | 100.56  | 90.00     | 447.99          | 11.039         | 11.037           | 5.85                | 2.149        |
| Oc$^{2+}$:Fe$^{2+}$ | 5.183 | 8.999 | 9.858 | 90.01    | 100.66  | 89.96     | 451.89          | 12.207         | 12.268           | 6.2                | 2.632        |
| Oc$^{2+}$:Fe$^{3+}$ | 5.186 | 8.989 | 9.852 | 90.91    | 100.43  | 89.90     | 451.64          | 10.993         | 12.268           | 5.85                | 2.632        |
| Oc$^{3+}$:Fe$^{2+}$ | 5.195 | 9.005 | 9.870 | 89.78    | 100.41  | 89.95     | 452.33          | 11.019         | 11.109           | 5.85                | 2.632        |
| Oc$^{3+}$:Fe$^{3+}$ | 5.195 | 9.006 | 9.8446| 89.73    | 100.43  | 89.97     | 453.11          | 10.993         | 12.268           | 5.85                | 2.632        |
| tt:Fe$^{2+}$ | 5.193 | 9.028 | 9.898 | 90.81    | 101.22  | 90.19     | 455.09          | 11.127         | 11.189           | 5.85                | 3.449        |
| tt:Fe$^{3+}$ | 5.193 | 9.028 | 9.898 | 90.81    | 101.22  | 90.19     | 455.09          | 11.127         | 11.189           | 5.85                | 3.449        |

The electronic structure of phlogopite crystals. In particular, the volume changes of the octahedra and tetrahedral where the Fe defects take place are directly related to the changes in the bond lengths between Mg and O to Fe and O atoms (see more details in the supporting information).

We now analyze the bandgap of phlogopite crystals without and with Fe ions. Figure 4 presents the density of states (DOS) of phlogopite crystal considered in figure 3. The electronic structure of pristine phlogopite is displayed in figure 4(a). Panels I and IV in figure 4(a) show the total DOS of pristine phlogopite $\text{Mg}_x\text{Al}_{y}\text{Si}_z\text{O}_{20}(\text{OH})_4\text{K}_2$. The valence band edge in pristine phlogopite is mainly composed by $\text{O}$ $p$-states, while the conduction band edge is mainly composed by states from $\text{O}$ ($\sim$34%), $\text{K}$ ($\sim$30%), and $\text{Mg}$ ($\sim$18%) (see supporting information for more details on the pristine phlogopite electronic structure). The bandgap of pristine phlogopite, calculated by using Scuseria–Ernzerhof hybrid functional (HSE) is approximately 7.0 eV (panel I in figure 4(a)), in good agreement with experimental evidence in synthetic phlogopite [70]. The partial DOS of the $\text{Mg}$ atom, the $\text{O}$ atoms bound to $\text{H}$ (from the $\text{OH}$) and to $\text{Mg}$ atoms, [H]–$\text{O}$–[Mg], and the $\text{O}$ atoms bound to $\text{Mg}$ atoms only [Mg]–$\text{O}$–[Mg] of the octahedron site $\text{Oc}^1$ are presented in the panels II–IV, respectively (see the labels above the graphics). The contribution of the $s$ and $p$ orbitals are also indicated in these graphics, by red and green lines, respectively, and their sum in black lines. Panels VI–VIII in figure 4(a) reveal the analyzes for the octahedron $\text{Oc}^2$ site.

Panels I and IV in figure 4(b) present the electronic structure of $\text{Mg}_x\text{Fe}_y\text{Al}_{z}\text{Si}_t\text{O}_{20}(\text{OH})_4\text{K}_2$ resulting due to the isovalent substitution of $\text{Mg}^{2+}$ by $\text{Fe}^{2+}$ ion in the $\text{Oc}^1$ and $\text{Oc}^2$ sites, respectively. The $\text{Fe}^{2+}$ ion induces similar electronic structure modification, regardless in the $\text{Oc}^1$ (panels II–IV) or $\text{Oc}^2$ (panels VI–VIII) sites, introducing $d$-$\text{Fe}$ ($d$-states are indicated by blue lines in figure 4(b)) and $p$-$\text{O}$ states, within the pristine phlogopite bandgap, in the same energy range, due to the $\text{Fe}$-$\text{O}$ bonding formation. As a consequence, the phlogopite bandgap is strongly reduced, becoming equal to 3.55 eV. This value is in agreement with our experimental observation (inset in figure 2(c)). Panels I and IV in figure 4(c) represent the electronic structure of $\text{Mg}_x\text{Fe}_y\text{Al}_{z}\text{Si}_t\text{O}_{20}(\text{OH})_4\text{K}_2$ resulted from the substitution of $\text{Mg}^{2+}$ by $\text{Fe}^{3+}$ ion in the $\text{Oc}^1$ and $\text{Oc}^2$ sites, respectively. In these cases, the hybridization of the $d$-$\text{Fe}$ and $p$-$\text{O}$ orbitals occurs mainly near the conduction band edge. The reduction of the phlogopite bandgap is smaller than in the case of $\text{Fe}^{3+}$ ions at the octahedra, becoming equal to 5.85 eV.

Panel I in figure 4(d) displays the DOS of pristine phlogopite, whereas panels II–IV show the partial DOS of the $\text{Al}$ atom, the $\text{O}$ atoms bound to $\text{Si}$ and the $\text{Al}$ atoms, [Si]–$\text{O}$–[Al], and the $\text{O}$ atoms bound to $\text{Mg}$ and the $\text{Al}$ atoms only [Mg]–$\text{O}$–[Al] of the tetrahedron site tt, respectively (see the labels above the graphics). Panels V–VIII in figure 4(d) reveal the details of the electronic structure of the corresponding sites in the $\text{Mg}_x\text{Al}_{y}\text{Si}_t\text{O}_{20}(\text{OH})_4\text{K}_2$ geometry, resulting due to the isovalent substitution of $\text{Al}^{3+}$ by $\text{Fe}^{3+}$ ion in phlogopite, at the tetrahedron site tt. The presence of $\text{Fe}^{3+}$ ions in the tetrahedral site leads to bonding between $d$-$\text{Fe}$ and $p$-$\text{O}$ orbitals, introducing states mainly near to the conduction band edge. The modifications in the electronic structure of phlogopite resemble that observed in the case of $\text{Fe}^{3+}$ in the octahedral sites $\text{Oc}^1$ and $\text{Oc}^2$. In the latter cases ($\text{Fe}^{3+}$ in $\text{Oc}^1$ and $\text{Oc}^2$ sites), two new narrow bands formed by $d$-$\text{Fe}$ and $p$-$\text{O}$ states are near the conduction band edge. While in the former ($\text{Fe}^{3+}$ in tt site), the corresponding new band closest to the conduction band edge is wider in energy (see the supporting information for more details on the electronic structure of these bulk compounds, as bandgap per spin channel, and partial DOS for all atoms). Therefore, our results reveal that the substitution of $\text{Mg}^{2+}$ by $\text{Fe}^{3+}$ ions is the main responsible for the reduction of the effective optical bandgap in phlogopite. In the supplementary information, we show DFT results on 1L-phlogopite, demonstrating that its bandgap gets narrower with reducing the number of layers, from 7 eV in bulk, down to 6.2 eV in the 1L limit. This reduction is attributed to the interaction between the $\text{K}$ and the $\text{O}$ atoms from the tetrahedral layer, which becomes stronger in comparison to the interaction in the bulk form. In addition, the effects of $\text{Fe}^{2+}$ ions in the $\text{Oc}^1$ and $\text{Oc}^2$ sites in to the 1L-phlogopite electronic structure and geometry.
Figure 4. First-principles calculation of bulk Fe:phlogopite structures. Electronic structure of (a) pristine, (b) Oc\textsuperscript{1}:Fe\textsuperscript{2+} and Oc\textsuperscript{2}:Fe\textsuperscript{2+}, (c) Oc\textsuperscript{1}:Fe\textsuperscript{3+} and Oc\textsuperscript{2}:Fe\textsuperscript{3+}, and (d) pristine and tt:Fe\textsuperscript{3+} phlogopite crystals. The graphics in panels I and V present the total DOS of phlogopite crystals. Contribution of the atoms in the octahedral sites Oc\textsuperscript{1} and Oc\textsuperscript{2}, Mg, Fe and O, and of atoms in the tetrahedron site tt, Al, Fe and O are indicated in the adjacent panels, where red, green and blue lines indicate the orbital contribution of s, p and d-states, and their sum are indicated by black lines, respectively. States below (above) the horizontal gray line are occupied (empty) and the up (down) spin-polarized states are represented as positive (negative) DOS. The calculations were performed by using HSE hybrid exchange-correlation functional.

are also investigated, showing similar trends to the bulk results.

In the following, we use the fact that phlogopite has weak van der Waals forces between the layers and strong in-plane bonds \[24\] to apply the mechanical exfoliation technique \[1\] for obtaining ultrathin slabs. Figure 5(a) and (b) shows the optical image of several phlogopite (hBN) flakes obtained by direct exfoliation of a bulk-crystal onto SiO\textsubscript{2}/Si.

The apparent color of the flake under the optical microscope depends on its thickness \[75\]. The lateral flake-size depends directly on the exfoliation process (scotch tape repetition), then, it may vary from sample to sample. However, it is possible to identify flake sizes varying from hundreds of nanometers up to hundreds of microns. Moreover, the flake-thickness follows the same behavior, but one can identify flakes ranging from about 1 nm thick
(thickness of an expected [28, 33] 1L) up to hundreds of nanometers (see more details in the supporting information). It is known that LMs are able to conform to the topography of the underlying substrate [76–78], hence, we perform topographical analysis of the exfoliated flakes using AFM (see section 4 for details). We identify that, as for hBN [77], phlogopite shows atomically flat (root mean square (rms) roughness, $R_{\text{rms}} < 0.2$ nm) surfaces over large areas. Figures 5(c) and (d) shows AFM topography images measured on phlogopite (58 nm thick) and hBN (54 nm thick) flakes, respectively. The average roughness measured in our samples are $R_{\text{rms}} = (0.17 \pm 0.03)$ nm (phlogopite) and $R_{\text{rms}} = (0.12 \pm 0.02)$ nm (hBN). These results indicate that phlogopite crystals show good surface topography and could potentially be embedded in vdWHs. Furthermore, the large area of these nanometer-thick phlogopite sheets, comparable to one of the exfoliated hBN slabs, makes it promising candidates for use not only as substrates in LM-based devices but also as insulator barriers in planar tunnel junctions or as dielectrics in field-effect transistors and nanocapacitors. Also, phlogopite presents a DC dielectric constant similar to hBN, as well as a lower refractive index with in-plane and out-of-plane anisotropies, all of which can be exploited for exciton- and plasmon-based vdWHs in nanophotonic and optoelectronic devices.

After the mechanical exfoliation, we have also investigated the stability of phlogopite under thermal annealing in air and in H$_2$/Ar atmosphere (see section 4 for details). The stability of the LMs in air is a crucial processing issue since it allows the manipulation of the materials without the need of sealed glovebox systems, making it easier to handle [79]. Moreover, understanding if the LMs are stable under a certain temperature is also crucial for vdWHs fabrication because the LMs are often annealed either in air or gas atmosphere for both cleaning the material surface and ensure the best layer-to-layer and layer-to-substrate adhesion, eliminating a substantial portion of air pockets (bubbles) on the interfaces between the constituent layers. Figures S9(a) and (b) presents the optical images of the flakes submitted to thermal annealing in oxidizing and reducing atmospheres, respectively. Whereas figures S9(c) and (d) shows the Raman and absorption spectra of the bulk-phlogopite crystal, respectively. The results demonstrate that phlogopite flakes, including 1L-phlogopite (figure S8), are well-stable at least up to 300 °C (maximum temperature analyzed in this work) and show no signs of topography and structural alteration. It is also important to stress that the flakes were left in ambient conditions for at least 13 months and exhibited no signs of degradation. For instance, figures S9(c) and (d) brings the Raman and absorption spectra, while figures S10(a)–(c) shows the optical and AFM images, as well as the XRD diffractogram, respectively, for fresh obtained material and after being left under open environment, corroborating with the structural stability of phlogopite. Therefore, our results suggest that phlogopite is strongly stable.
under ambient environment and thermal process, which is a good requirement for LMs-based applications. However, we must stress that at this moment we cannot exclude the existence of water molecules adsorbed at the material surface or the presence of charge trapping that could induce hysteresis on field effect transistor (FET) applications [80–84].

We now focus on the use of this material as atomically flat substrates in vdWHs. Several works have shown that the underlying substrate affects the excitonic emission in monolayer transition metal dichalcogenides (1L-TMDs), thus changing the optical performance of the devices designed [85–89]. Figures 5(c) and (f) shows optical images of the transferred 1L-WS₂/phlogopite and 1L-WS₂/hBN materials, respectively (see section 4 for description details regarding the vdWHs fabrication). For clarity, the optical images have false color contrast, hence, one can distinguish the 1L-WS₂ flakes from the underlying LMs. The 1L-WS₂ flakes are intentionally deposited partially over the LMs and SiO₂, thus, we can directly compare the effect of the underlying LM to the SiO₂/Si region. Thereafter, PL spectroscopy is applied to investigate the effect of the substrate on the PL emission of 1L-WS₂ (see section 4 for details). Figure 6(a) plots the representative PL spectra for 1L-WS₂ at room temperature on the different substrates.

The normalized spectra show the characteristic features from 1L-WS₂ close to 617 nm (2.01 eV) and 630 nm (1.97 eV). These signatures are commonly associated with the emission from neutral exciton (X⁰) and negatively charged trions (X⁻) because both exciton species can coexist at room temperature [85–88]. The findings in figure 6(a) indicate that the underlying substrate affects the X⁻ emission. By fitting the data with Lorentzian functions, we extract quantitative information about the X⁰ and X⁻ emissions, as shown in figures 6(b) and (c). It is worth noticing that changes in position and spectral weight (X⁰/X⁻ integrated area ratio) of the peaks in the PL spectrum are affected by external doping [90]. On the one hand, no significant variations are observed for the position of both peaks, suggesting no changes in the bandgap and exciton binding energy of 1L-WS₂ by the LM-substrate [91]. The small shift of the PL peak position from sample to sample could be related to some strain induced by the PDMS transfer. Conversely, figure 6(c) shows a clear difference in the relative spectral integrated area ratio of exciton and trion (X⁰/X⁻). Normally, the formation of X⁻ suppresses the radiative recombination of X⁰ and thus reduces the X⁰/X⁻ PL ratio [90, 91]. Therefore, our results suggest that the SiO₂ substrate induces extra n-type doping to the 1L-WS₂ flakes, consequently, increasing the X⁻ formation. Whereas phlogopite flakes work similarly to hBN crystals, decreasing the contribution from the SiO₂, and favoring the radiative recombination (X⁰) most likely due to suppression of charge transfer from the SiO₂ surface [86, 87]. Our Raman data (figure S3(d)) performed on these samples show negligible changes to the Raman modes, suggesting no detectable introduction of extra doping coming from the phlogopite substrate. Note that all insulating flakes are initially selected by optical contrast followed by AFM characterization to confirm the thickness and surface quality. The thickness of all selected LM-substrate is in the range of 30–60 nm. This thickness selection is needed to decrease the effect of the charged puddles (trapped impurities) at the SiO₂ surface that is known to affect the electronic properties of the LMs [85–88]. Consequently, our results suggest that such material thickness is enough to improve the X⁰ recombination efficiency of 1L-TMDs. Although low-temperature measurements are not performed and it is out-of-scope of our work, further experiments (electrical and optical) using phlogopite as dielectric substrate in low-temperature gated-PL (FET architecture) will be employed to understand the influence of the Fe impurities to the electronic properties of the transferred and active 1L-TMD. Finally, we must highlight that all features discussed in our work (large bandgap material, ultrathin layers, atomically flat surface, and air stability) would make phlogopite a promising candidate for using in ultrathin and flexible low-cost LM-based optoelectronic devices.
3. Conclusion

We systematically studied the basic properties of ultrathin phlogopite crystals by means of XRD, XRF mapping, WDS, EPR, UV–vis, AFM, FTIR, Mössbauer, Raman, and DFT calculations. We showed that mono- and few-layers of this material are air and temperature stable, are easily obtained by standard mechanical exfoliation technique, and have atomically flat surface. Moreover, our results confirmed that natural phlogopite presents Fe ions in its lattice and this explains the reduction observed for its optical bandgap (down to 3.6 eV). Nevertheless, the existence of external impurities could boost its use on defect engineering for localized luminescence experiments. We then fabricated ultrathin 1L-WS₂/phlogopite heterostructures and demonstrated that the X⁰ recombination efficiency is at least three-fold higher than on SiO₂ substrates, similarly to those obtained on 1L-WS₂/hBN heterostructures. Finally, the present proof-of-concept study shows that phlogopite can be easily exfoliated down to mono- and few-layers with large areas (thousands of µm²), concluding that this mineral should be regarded as good and promising candidate for LM-based applications as a low-cost layered nanomaterial.

4. Methods

X-ray diffraction: The experiments were acquired in a commercial diffractometer (XRD Rigaku, Miniflex II) with Cu-Kα radiation (λ = 1.5418 Å), using a four-crystal monochromator and collimating slits in the Bragg–Brentano geometry (θ:2θ). The generator voltage and current were set to with 30 kV and 15 mA, respectively. For acquiring the diffractogram a powder sample was made from the mechanical grind of a large crystal (inset in figure 1(a)).

Wavelength-dispersive spectroscopy: For the WDS measurements, a phlogopite sample was prepared on a resin support, polished and metalized with carbon. The quantitative microanalysis by WDS was performed for several points at different regions of the sample for a statistical quantification using a previously calibrated Jeol 8900 electron microprobe.

Synchrotron radiation x-ray fluorescence: Synchrotron radiation XRF mapping in an area of 250 × 250 µm² and 5 × 5 µm² was performed at room temperature with beam size down to 500 × 200 N m² using SDD 4 elements Vortex (Hitachi) detectors and excitation energy of 7.2 keV selected as the spectral region of interest for Fe K-alpha emission line with an energy resolution of ∆E/E = 10⁻⁴ at the Tarumā endstation/Carnauba beamline from the Sirius Synchrotron source. The XRF mapping images were analyzed by the PyMCA software [92]. The brighter red signal indicates the higher Fe concentration areas in phlogopite.

Electron paramagnetic resonance: For the EPR measurements, a custom build commercial Magnetech MiniScope MS 400 X-band spectrometer coupled to water-cooled electromagnets capable of producing magnetic fields up to 800 mT was used. The EPR angular dependence at at 75 K of a bulk phlogopite sample coupled to a goniometer was performed with c axis perpendicular to the rotating axis, in which the c axis will be parallel to the applied magnetic field for a specific orientation. The parameters used to acquire all spectra were 9.440(1) GHz with approximately 30 mW of power, 100 kHz of modulation, and 0.5 mT of field modulation. The EPR signals are labeled by their effective g values defined by the relation hν = gβB, where h is Planck’s constant, ν is the microwave frequency, β is the Bohr magneton and B is the modulus of the magnetic field.

Optical absorption: The absorbance spectrum and the reflectance spectrum needed to produce the Tauc plot were acquired with a Shimadzu 3600 Plus UV–vis–NIR spectrometer on a phlogopite bulk with dimensions (~0.1 × 5 × 10 mm³—thickness × width × length) fixed to the sample holder. This sample was carefully peeled off with tweezers from the crystal shown in figure 1. The grating change occurs at 720 nm for the spectral range from 250 to 1250 nm during the experiment.

Mössbauer spectroscopy: The Mössbauer spectrum was measured at 300 K in constant acceleration mode (triangular velocity) using a ⁵⁷Co source in Rh matrix. Phlogopite powder was pressed into a sample holder (Ø = 0.9 cm) to produce an area of ~0.6 cm². Sample thickness was close to the thin absorber approximation, to avoid thickness effects. The spectrum was fitted with Lorentzian doublets using Normos software [93]. The full width at half maximum considered for all doublets was 0.35 mm s⁻¹. The isomer shifts and quadrupole splittings were allowed to vary to adjust correctly the spectrum.

Raman and photoluminescence spectroscopy: The experiments were done in a confocal Raman microscope WITec Alpha 300R in the backscattering configuration. We used 488 nm excitation laser with a 100× objective which has a numerical aperture (NA) of 0.9. For the phlogopite Raman spectra, the laser power was kept constant at 10 mW during all measurements. Each Raman spectrum was collected with five accumulations of 60 s with a grating of 1800 grooves mm⁻¹. This procedure was repeated for the Raman measurements taken on the exfoliated phlogopite flakes onto SiO₂/Si substrate. For the PL measurements on the 1L-WS₂ flakes transferred to hBN and phlogopite, we used 100 µW to avoid damaging of the 1L-WS₂. Each PL spectrum was collected with three accumulations of 10 s with a grating of 600 grooves mm⁻¹. Several PL spectra were collected on the same sample (i.e. 1L-WS₂ partially transferred onto the LMs) to check uniformity and different LMs of each insulator were used to
estimate the impact of the underlying substrate to the PL emission. The data presented in figures 6(b) and (c) were averaged considering 15 PL spectra of each material. Previously to all measurements, the 488 nm laser was aligned on a prime silicon wafer, using the Si peak at 521 cm$^{-1}$ as reference. For the Raman measurements on the 1L-WS$_2$ flakes transferred to hBN and phlogopite substrates, we used 500 µW to avoid damaging of the 1L-WS$_2$. Each Raman spectrum was collected with three accumulations of 60 s with a grating of 1800 grooves mm$^{-1}$.

**Fourier-transform infrared spectroscopy:** The micro-FTIR measurements were carried out in a Cary 620 FTIR microscope from Agilent Technologies using a Globar source with 8 cm$^{-1}$ of spectral resolution. Due to the non-transparency of the sample, single-point spectra in reflectance mode of a crystal fragment from the bulk phlogopite sample placed atop a flat gold surface were recorded by a MCT detector and a 25 × objective lens with approximately 400 × 400 µm$^2$ of spot size. The final spectrum is an accumulation of 64 scans normalized by the spectrum of a clean Au surface as background reference.

**Exfoliation and assembly of the van der Waals heterostructures:** For the assembly of the vdWHs we have used the following procedure: (a) phlogopite and hBN bulk-crystals were mechanically cleaved [1] individually by scotch tape onto 285 nm SiO$_2$/Si substrates. The insulating LMs were initially checked under the optical microscope (bright and dark field) followed by AFM characterization to confirm the thickness and surface quality (e.g. free of contaminants, residues of glue or other impurities) and imperfections (e.g. layers missing or cracks). (b) WS$_2$-bulk crystal (sourced from HQ Graphene) was exfoliated by scotch tape, then, exfoliated again on a polydimethylsiloxane (PDMS) stamp placed on a glass slide for inspection under an optical microscope. Optical contrast was used to identify 1L-WS$_2$ prior to transfer [94], followed by PL characterization. (c) The selected 1L-WS$_2$ flakes onto the PDMS stamp were then aligned on the designated phlogopite (or hBN) flakes and stamped using xyz micromanipulators [95].

**Atomic force microscopy:** The AFM experiments were obtained with a Bruker Dimension Icon system operated in tapping mode. To characterize all samples, the thickness and roughness of the crystal’s slabs were estimated from the topography images collected in 5 × 5 µm$^2$ scan area and with 512 scanlines under ambient conditions. The $R_{rms}$ values presented in this work were averaged based on at least five flakes of each material with a minimum flake thickness of 20 nm, decreasing, therefore, the roughness contribution coming from the SiO$_2$/Si substrates ($R_{rms} = (1.3 \pm 0.3)$ nm).

**Thermal annealing:** For the thermal annealing experiments, two approaches were pursued: (a) in air—the SiO$_2$/Si substrates with exfoliated crystals (hBN and phlogopite) were left on a standard hot-plate under ambient conditions for 1 h at 175 °C, followed by another 1 h at 300 °C. (b) In gas environment—distinct SiO$_2$/Si substrates with exfoliated crystals (hBN and phlogopite) were inserted into a quartz tube in a tubular furnace at 25 °C. Thus, we set a gas flow of 90 sccm (Argon) and 300 sccm (H$_2$), a final temperature of 300 °C, and a temperature rate of 15 °C min$^{-1}$. The samples were left at 300 °C for at least 4 h before turning the heater off. Hence, the samples were cooled down to 100 °C with continuous flow before opening the furnace lead and closing all gases off.

**Ab initio simulations:** First-principles simulations were performed by using spin-polarized DFT [96, 97] as implemented in the Quantum ESPRESSO distribution [98, 99]. The valence electron–ion interactions were considered by using norm-conserving pseudopotentials [100] (pseudopotentials files H.pz-mt_fhi.UPF, K.pz-mt_fhi.UPF, Mg.pz-mt_fhi.UPF, Fe.pz-mt_fhi.UPF, Al.pz-mt_fhi.UPF, Si.pz-mt_fhi.UPF, and O.pz-mt_fhi.UPF, available at [101]). The exchange-correlation energy is evaluated within the Perdew–Zunger’s LDA for geometry optimization calculations and within Scuseria–Ernzerhof hybrid functional (HSE) [102–105] for band structure calculations. 1L-Phlogopite calculations were carried by using proper 2D open boundary conditions [106], with images separated by approximately 24 Å of vacuum. Forces on the atoms and stress on the lattice are lower than 0.1 mRy bohr$^{-1}$ and 10 MPa, respectively. The plane-wave kinetic energy cutoff to describe the electronic wave functions (charge density) was set to 42 Ha (168 Ha). The Brillouin zone integrations were performed within the Monkhorst–Pack scheme [107], by using $4 \times 2 \times 2$ (4 × 2 × 1) Gamma center k-point grids in the geometry optimization calculations for bulk (1L). The Brillouin zone integrations to evaluate the exchange operator were performed on additional $4 \times 4 \times 2$ (4 × 2 × 1) q-point grids [108–110] for bulk (1L) phlogopite.

**Data availability statement**

The datasets obtained and analyzed during the study are available from the corresponding authors on reasonable request.

**Code availability**

Scripts for the theoretical analyses are available from the corresponding authors on reasonable request.

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**Conflict of interest**

The authors declare no competing interests.

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