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Synchrotron radiation FT-IR micro-spectroscopy of fluorophlogopite in the O–H stretching region

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Abstract

Synchrotron radiation FT-IR polarized micro-spectroscopy has been used to investigate the natural mica fluorophlogopite in order to characterize the stretching vibrations of the OH groups and their orientation relative to the mica cleavage (0 0 1) plane. A procedure to eliminate undesired interference fringes, typically observed when working with thin single-crystals, was set up using an ad hoc sample preparation, and tested.

The naturally high brilliance and high polarization properties of synchrotron radiation allows to study very small flakes and hence offers new analytical possibilities in comparison to conventional powder FT-IR spectroscopy.

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Keywords: Infrared; Synchrotron radiation; Mica; Microscopy; Phyllosilicates

1. Introduction

Micas are phyllosilicates in which the unit structure (*TOT* layer) consists of one octahedral sheet sandwiched between two opposing tetrahedral sheets [1]. Successive layers are separated by planes of non-hydrated interlayer *I* cations. The interlayer bonds are very weak, so that the stacked layers sequence determines the cleavage plane of micas to be parallel to (0 0 1). As a result, cleaved mica crystals are thin blades that can be reduced down to a thickness of a few tens of μm .

In the mica layer, octahedra and tetrahedra share corners and these corners are oxygen atoms. By contrast, two anion sites of the octahedral sheet that are shared only by other octahedra are made of oxygen atoms bound to hydrogen so as to form OH groups (see Fig. 1), when not of other anions such as F and Cl. The hydrogen atom electrostatically interacts with its neighbouring atoms, so as to affect both the direction and the vibration frequency of the O–H bond, which is typically in the $3200\text{--}3700\text{ cm}^{-1}$ range. Generally speaking, substitution of atoms in the octahedral and/or tetrahedral sheets induces local

distortions. At certain concentrations, which depend on the atomic substitution, these distortions may induce effects into the whole mica structure, resulting in different orientations of the OH groups and of their vibration frequencies because of the different space charge distributions around them. Thus, knowledge of the orientation of the OH group with respect to the mica (0 0 1) plane may provide insight of the crystal-chemical structure of these phyllosilicates.

2. Experimental

The OH groups are hardly detectable by X-ray diffraction or by spectroscopic methods based on X-rays. By contrast, FT-IR spectroscopy is a relatively simple technique, extremely sensitive to OH stretching vibrations. Moreover, when working with mica crystals and using linearly polarized light and an IR microscope and while keeping constant control on the investigated area (typically of the order of $200\text{ }\mu\text{m}$ of diameter or less), one can easily probe by FT-IR different crystallographic orientations simply by tilting the sample with respect to direction of the electric field vector, thus highlighting the angular dependence of the OH group absorption bands [2]. The major drawback of FT-IR micro-spectroscopy on mica blades is the presence of

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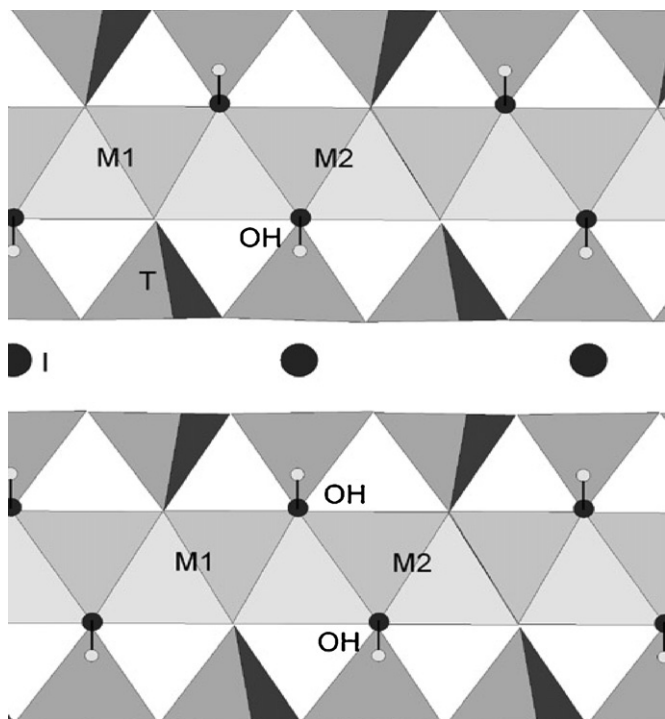


Fig. 1. Typical trioctahedral mica structure as seen from the (1 0 0) direction. In the image are indicated the (Si, Al) tetrahedra (T), Mg-containing octahedra (M1, M2), the interlayer cations (I) and the OH groups.

interference fringes, due to the natural parallelism of the two mica–air interfaces, which superimposes onto the vibrational spectra. This is particularly evident in mica samples with thickness in the range 8–500 μm . In order to remove this unwanted contribution, we tested and optimised a method that allows removing the coherent interference due to the parallelism of the mica surfaces. It consists in depositing a suitable material (for example, CsI), transparent to mid-IR radiation, on one

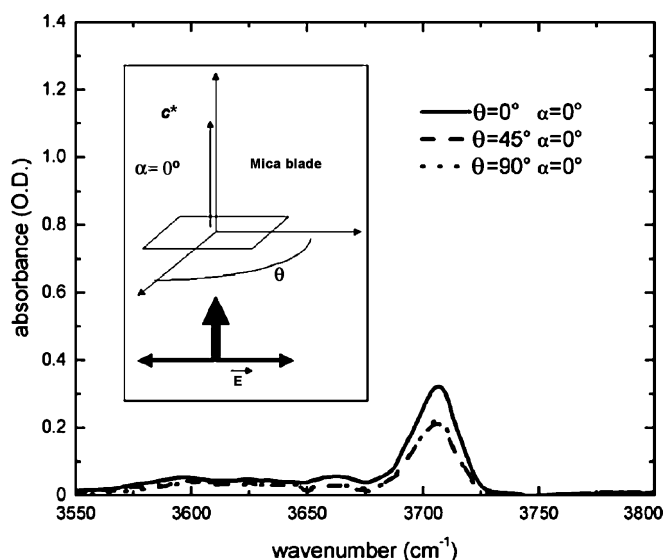


Fig. 2. Infrared absorption spectra of a natural fluorophlogopite crystal in the OH stretching region; the sample was placed and rotated as shown in the inset ($\alpha = 0^\circ$, $\theta = 0-90^\circ$) with respect to the IR synchrotron linearly polarized light beam.

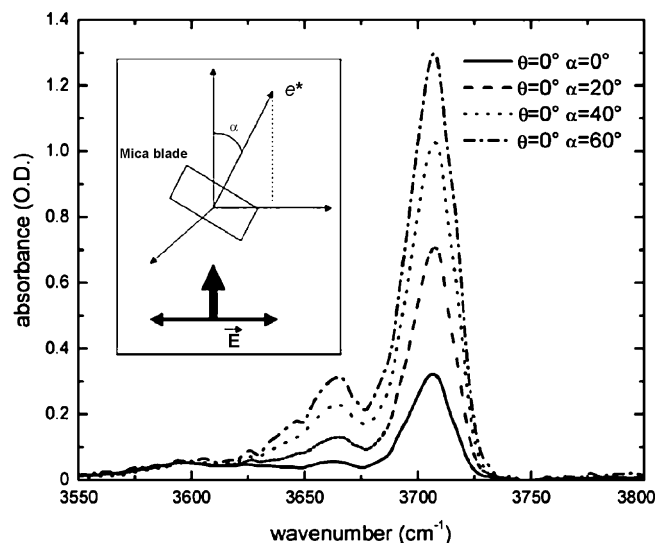


Fig. 3. Infrared absorption spectra of a natural fluorophlogopite crystal in the OH stretching region; the sample was placed and rotated as shown in the inset ($\alpha = 0-60^\circ$, $\theta = 0^\circ$) with respect to the IR synchrotron linearly polarized light beam.

surface of the analysed crystal. In this way, we were able to modify the roughness and the planarity at the interface between air and mica, so that interference fringes could be eliminated from the spectrum. The main advantage of this method is in the possibility of collecting data at high resolution (4 cm^{-1} or less). However, even if the material is deposited on all the mica surface, total fringe elimination was found to take place only on some areas with a diameter in the range 30–150 μm . Consequently, on such small areas, a powerful source like synchrotron radiation is needed in order to achieve a good signal-to-noise ratio in reasonable acquisition times. Actually, by reducing the sample thickness down to the range of 2–6 μm , the interference fringes period becomes much greater than the OH absorption bandwidth and the above treatment is not necessary, but generally the OH absorption band of micas at such a small thickness is not strong enough to be studied with acceptable accuracy. On the contrary, for certain micas it was necessary to investigate samples having thickness just less than 6 μm , to avoid saturation of the OH group absorption. These micas were investigated simply by looking at the sample borders, because it proved to be almost impossible to produce and manipulate mica blades that were large enough laterally, but with a thickness of only a few μm . In this case cleaved mica borders had typically a width of $\sim 20 \mu\text{m}$ and the thickness was estimated by the interference fringes period.

All experiments were performed at the SINBAD beamline using the IRSR source of the DAΦNE storage ring complex of INFN, Laboratori Nazionali di Frascati. At SINBAD, a Bruker Equinox 55 interferometer, modified to work in vacuum, and an IRscope I microscope is installed at the end of the synchrotron beam line. SINBAD is a very brilliant source due to the high electron current (up to 1.8 A) circulating in the ring at energy 0.51 GeV [3]. A KRS-5 linear polarizing filter with 95% polarization degree in the mid-IR range was placed before the sample and a MCT detector cooled at liquid nitrogen temperature was installed on the microscope. We recorded a

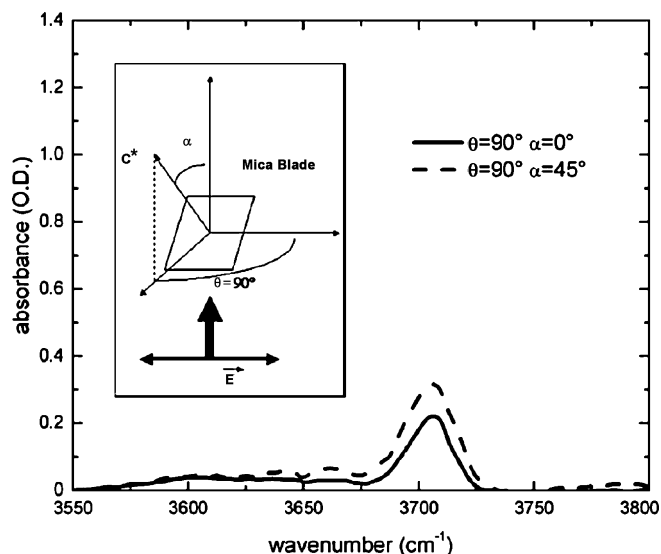


Fig. 4. Infrared absorption spectra of a natural fluorophlogopite crystal in the OH stretching region; the sample was placed and rotated as shown in the inset ($\alpha = 0\text{--}45^\circ$, $\theta = 90^\circ$) with respect to the IR synchrotron linearly polarized light beam.

series of spectra, at a resolution of 4 cm^{-1} , after rotating cleaved natural mica blades around the horizontal and vertical axes. This allowed changing the projection of the OH group along the electric field vector, whose direction with respect to the microscope sample stage is known (see insets of Figs. 2–4).

Sample orientation is defined by two angles: α is the angle between the c^* axis (defined as the axis perpendicular to the mica basal 001 plane) and the light propagation direction (vertical); θ is the angle between the projection of c^* on the horizontal plane (microscope stage) and the IR beam electric field vector direction. In this paper, we show and discuss the results obtained on a natural fluorophlogopite from Franklin (NJ, USA), ideally $\text{KMg}_3[\text{Si}_3\text{AlO}_{10}\text{F}_{1.3}(\text{OH})_{0.7}]$, having a thickness of $\sim 50\text{ }\mu\text{m}$, whose surface was treated as explained before in order to remove interference fringes. More details about this sample can be found in Refs. [1,4].

3. Results and discussion

The mica blade was first positioned horizontally on the microscope stage in what was defined as the initial position, i.e. $\theta = 0^\circ$ and $\alpha = 0^\circ$. The absorbance FT-IR spectrum showed one main component peaked at 3705 cm^{-1} and a much weaker component at 3664 cm^{-1} . Then, the sample was turned clockwise around the vertical axis so that θ increased from 0° to 90° (Fig. 2). Both absorption bands remained almost unchanged. After rotating the sample back to the initial position, θ was kept to 0° and only α was changed, increasing from 0° to 60° (Fig. 3). During this second rotation the absorption intensity of both bands increased. After turning the sample back to the initial position and rotating it to a position corresponding to $\theta = 90^\circ$ and $\alpha = 0^\circ$, we increased α from 0° to 45° . During this third rotation both absorption bands showed very small modifications (Fig. 4).

The crystal-chemical formula of the analysed fluorophlogopite sample is (neglecting minor constituents): $(\text{K}_{0.77}\text{Na}_{0.16}\text{Ba}_{0.05})\text{Mg}_{3.00}(\text{Si}_{2.95}\text{Al}_{1.05})\text{O}_{10}\text{F}_{1.30}(\text{OH})_{0.70}$ [5]. On the basis of this formula we can model the absorption bands observed in the OH-stretching spectrum in terms of the local NN (nearest-neighbour) and NNN (next-nearest-neighbour) configurations around the O–H group. In particular, the main component at 3705 cm^{-1} can be assigned to an OH dipole bonded to a trimer of octahedra occupied by Mg and directed toward a Si_4Al_2 tetrahedral ring; this configuration can be expressed as $\text{MgMgMg}\text{--OH}\text{--Si}_4\text{Al}_2$ and has the highest probability of occurrence, in agreement with its intensity. In phlogopite, the presence of three divalent octahedral cations in the first coordination shell of the OH group is such that the O–H dipole is involved in a very weak hydrogen-bond interaction with the surrounding environment, as testified by the relatively high frequency of vibration (3705 cm^{-1}); this being the case, the O–H vector is aligned along the c^* direction [6,7]. The crystal-chemical formula given above shows that divalent Mg is the only octahedral cation in the structure and that there is a slight Al excess at the tetrahedral sites. The second band in the spectrum, at 3664 cm^{-1} can be thus assigned to an O–H dipole directly bonded to the same octahedral configuration as the 3705 cm^{-1} component, but locally pointing toward a Si_3Al_3 tetrahedral ring [8]. In such a situation the O–H vector is not expected to deviate significantly from the direction perpendicular to the octahedral sheet (c^*), and this interpretation is confirmed by the fact that both bands in Fig. 3 show the same polarization behaviour.

4. Conclusion

The present study shows that FT-IR polarized-light microscopy allows to characterize the stretching vibrations of the OH groups and their orientation relative to defined crystallographic elements (for instance the basal 001 plane) of layer-structured natural crystals.

This technique, exploiting the naturally high brilliance and high polarization properties of synchrotron radiation, provided it is associated with an ad hoc sample preparation, can eventually provide much more detailed information than previously obtainable using conventional FT-IR spectroscopy on powder samples, as most phyllosilicates are, where linear polarized experiments are neither obvious nor effective. Moreover, such a technique can be applied to similar spectroscopic studies on two-dimensional samples.

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