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High-resolution imaging of (100) kyanite surfaces using friction force microscopy in water

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ABSTRACT

In this paper, we present high-resolution friction force microscopy (FFM) images of the (100) face of kyanite (Al_2SiO_5) immersed in water. These images show an almost rectangular lattice presumably defined by the protruding oxygen of AlO_6 polyhedra. Surface lattice parameters measured on two-dimensional fast Fourier transform (2D-FFT) plots of recorded high-resolution friction maps are in good agreement with lattice parameters calculated from the bulk mineral structure. Friction measurements performed along the [001] and [010] directions on the kyanite (100) face provide similar friction coefficients $\mu \approx 0.10$, even if the sequences of AlO_6 polyhedra are different along the two crystallographic directions.

1. Introduction

Kyanite, Al_2SiO_5, is an important metamorphic nesosilicate, which is commonly found in rocks formed in ancient and present subduction zones [1,2]. This mineral is the high-pressure polymorphous of the aluminium silicate group with formula Al_2SiO_5 (i.e., sillimanite, andalusite and kyanite). This group of minerals has been used by petrologists from long time ago to estimate pressure and temperature metamorphic conditions on the basis of their phase diagram. However, the use of the Al_2SiO_5 phase diagram to infer metamorphic conditions is problematic due to the high metastabiliy of all three mineral structures, which persist for long periods of time under P-T conditions far from equilibrium [3]. The metastability of Al_2SiO_5 minerals is mainly due to the fact that transformations from one mineral to another are reconstructive and they involve breaking strong Si–O and Al–O bonds [4]. In the case of kyanite, the arrangement of Si–O and Al–O bonds seems to be not only responsible for its metastability, but also for its remarkable hardness anisotropy. Therefore, the understanding of both the rheological properties of kyanite and its reactivity in geotectonic environments will be improved by conducting detailed crystallochemical studies of this mineral and, particularly, of its surfaces.

The main industrial use of kyanite is in refractory industry as a raw material to produce mullite, an important refractory mineral. Mullite is a rare mineral that only appear in a few uneconomical mineral deposits in the world [5]. The industrial process to produce mullite from Al_2SiO_5 minerals is through calcination at temperatures higher than 1000 °C [6]. Kyanite has the lowest temperature decomposition of the three Al_2SiO_5 minerals, and therefore, it is the most suitable to produce mullite [6]. Kyanite is also used in abrasive and electrical industries. Nowadays, new studies in kyanite applications propose other applications, such as its use to obtain metallurgical alumina [7]. Both the development and improvement of new industrial uses of kyanite also requires a better understanding of its crystallochemical surface properties.

In this work, we show first images and friction measurements of kyanite (100) surfaces recorded using a friction force microscopy (FFM) operating in contact mode in water. This technique was used in previous works by our group to obtain images with molecular resolution of mineral surfaces, organic molecules grown on minerals and organic crystals [8–12]. In addition, this method allows us to obtain friction coefficients between probing tips and surfaces along different crystallographic orientations. Both high-resolution images and friction coefficients obtained in this paper are discussed on the basis of the structural features of kyanite (100) surface.

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2. Materials and methods

2.1. The kyanite sample

Kyanite crystallises in the triclinic $P\bar{1}$ space group with the following cell parameters: $a = 0.71$ nm, $b = 0.79$ nm, $c = 0.56$ nm, $\alpha = 89.99°$, $\beta = 101.15°$, $\gamma = 105.95°$ and Z = 4 [13]. Kyanite structure can be described as formed by chains of edge-sharing AlO_6 and SiO_4 polyhedra running along the *c* axis (Fig. 1). This orientation of the chains of AlO_6 and SiO_4 polyhedra can be related to the different hardness of kyanite, measured on different crystallographic planes. Hence, the hardness of kyanite in Mohs' scale is ≈ 7 for [100] and [010] and ≈ 5 for [001]. Exfoliation of kyanite crystals along the (100) and (010) faces are perfect and poor, respectively. Along the (001) plane no exfoliation occurs. The combination of these three faces results in typical fibrous habit of kyanite [14].

The sample used in this work was a kyanite from Brazil. The sample was confirmed to be kyanite (PDF number 11-0046) by X-ray powder diffraction conducted with a Siemens D-500 diffractometer, equipped with a Cu-Kα radiation source.

2.2. Friction force microscopy (FFM)

The study presented here was performed using a commercial AFM (Nanoscope Multimode IIIa, Veeco Instruments), equipped with a ~15 × 15 μm^2 scanner and a closed fluid cell. Kyanite crystals were freshly cleaved along (100) faces with a razor blade and placed in the AFM fluid cell. Then, deionised water (Mili-Q, 18 MΩ · cm) was injected into the fluid cell. Both observations and data collection were carried out at room temperature operating in contact mode while recording height and lateral deflection signals. Scan areas ranged from 2 × 2 μm^2 to 10 × 10 nm^2, and the scan rates varied from ~5 Hz to ~61 Hz. In all the cases, 512 lines per scan were recorded. Supersharp tips mounted on triangular cantilevers (Bruker SNL-10 D) were used for acquiring high-resolution images.

Lateral deflection signals recorded with the AFM were used to map the friction forces while scanning square areas along the [010] and [001] directions on kyanite (100) faces at different loading forces. The experiments were carried on by applying increasing-decreasing cycles of normal force. The equation used to calculate lateral forces was as follows [16]:

$$F_L = \frac{3h}{2L} \times k_T \times S \times V_L \quad (1)$$

where *h* is the height of the tip and half of the cantilever thickness, *L* is the length of the cantilever, k_T is the torsional spring constant of the cantilever (calculated following Noy et al. [17]), *S* is the sensitivity of the photodetector in nm/V and V_L is the difference of the averaged trace and retrace signals (in Volts) divided by 2. The normal force was estimated as follows [16]:

$$F_N = S \times k_N \times V_N \quad (2)$$

where k_N is the normal spring constant and V_N is the set point value (in Volts). Both sharp silicon nitride (Bruker NP-10 D) and supersharp silicon nitride (Bruker SNL-10 D) tips were used for performing nanotribological measurements.

More than 100 AFM images were collected and analysed using the software developed by Nanoscope (5.30r3sr3) and Nanotec (WSxM) [18].

3. Results and discussion

3.1. High-resolution FFM images of kyanite (100) surface

When small areas (10 × 10 nm^2) of kyanite (100) surfaces are scanned almost parallel to the [010] direction, lattice resolved friction images are readily acquired. It is important to note that images with lattice resolution where obtained only when kyanite surfaces were fully immersed in water. This is mainly due to the fact that a homogeneous liquid environment eliminates capillarity forces (i.e., the formation of meniscus between the AFM tip and the surface), and the sliding process is not significantly perturbed by viscous forces [8–12]. As a result, the quality and resolution of recorded images is strongly improved.

The patterns observed in high-resolution friction images show an almost rectangular centred lattice defined by five maxima of the friction force (Fig. 2). The main directions on the (100) surface defined by the maxima are [010] and [001]. Since the angle between these directions is 89.99° [13], the surface unit cell is almost rectangular.

Maxima in friction maps can be interpreted as the result of stick-slip phenomenon between the tip apex and selected atoms protruding out of the scanned surfaces (e.g., Pina et al. [8]). This is clearly visible in the images corresponding to a series of complete forward and backward scans along the surfaces (Fig. 3A, B), and, especially, in the cross sections showing saw-tooth profiles corresponding to long stick and much faster slip phases (Fig. 3C).

In order to correctly identify the surface atoms which originate the friction maxima during the scan, we referee to the kyanite (100) surface structure sketched in Fig. 1. As can be seen in this figure, a number of

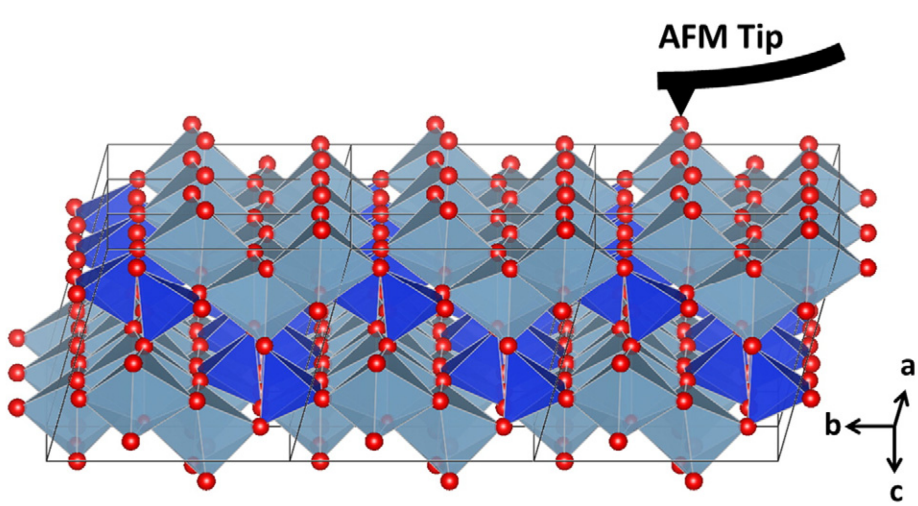

Fig. 1. Structure of kyanite. AlO_6 and SiO_4 polyhedra are represented in light and dark blue respectively. Oxygen are represented as red spheres. The top face is the (100) surface and the tip is represented on it. The *b* and *c* axes correspond to the [010] and [001] directions, respectively (structure projection made with Vesta [15]).