



Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

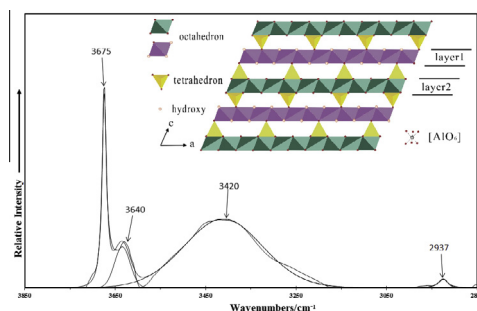
The molecular structure of chloritoid: A mid-infrared and near-infrared spectroscopic study

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HIGHLIGHTS

- Near-infrared spectroscopy was used to study the structure of chloritoid.
- The crystal structure of chloritoid was proposed.
- There is not exist water in the chloritoid crystal structure.
- There are two different octahedral layers in the structure of chloritoid.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 25 August 2014

Received in revised form 4 January 2015

Accepted 19 February 2015

Available online 7 March 2015

Keywords:

Chloritoid

Molecular structure

Infrared spectroscopy

ABSTRACT

The mineral chloritoid collected from the argillite in the bottom of Yaopo Formation of Western Beijing was characterized by mid-infrared (MIR) and near-infrared (NIR) spectroscopy. The MIR spectra showed all fundamental vibrations including the hydroxyl units, basic aluminosilicate framework and the influence of iron on the chloritoid structure. The NIR spectrum of the chloritoid showed combination $(\nu + \delta)_{\text{OH}}$ bands with the fundamental stretching (ν) and bending (δ) vibrations. Based on the chemical component data and the analysis result from the MIR and NIR spectra, the crystal structure of chloritoid from western hills of Beijing, China, can be illustrated. Therefore, the application of the technique across the entire infrared region is expected to become more routine and extend its usefulness, and the reproducibility of measurement and richness of qualitative information should be simultaneously considered for proper selection of a spectroscopic method for the unit cell structural analysis.

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Introduction

Chloritoid is a rock-forming mineral found in Al-rich metapelitic rocks. The mineral chloritoid was found in the bottom of Yaopo Formation of western hills of Beijing, China. Its chemical formula is

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$(\text{Fe}_{1.93}^{2+}\text{Mn}_{0.33}\text{Ti}_{0.06})\text{Al}_{3.92}\text{Si}_{2.11}\text{O}_{12.18}$ with unit cell parameters: $a = 9.48728 \text{ \AA}$, $b = 5.43418 \text{ \AA}$, $c = 18.11236 \text{ \AA}$, $\beta = 102.0191^\circ$, $z = 4$ (calculated in another paper) [1]. Different stacking polytypes of chloritoid occur in the nature, the two most abundant being are a two layer monoclinic one, $2M_2$, and a one-layer triclinic one, $1T$, (Jefferson and Thomas 1978) [2]. The two polymorphs are related to each other in such a way that the monoclinic cell can essentially be considered to contain two triclinic cells [3]. Moreover, non-random stacking disorders in the structure of chloritoid can be

clearly observed by High Resolution Electron Microscopic (HREM) [2]. Although a lot of work has been done to gain insight into the structure of chloritoid, there are still many open questions on its structure stability and crystal chemistry and few papers can be found about structure research of the mineral chloritoid.

Vibrational spectroscopy is one of the most important tools for investigating the structure of layered materials. Especially, near-infrared (NIR) and mid-infrared (MIR) spectroscopy have been considered as an alternative analytical method because they are fast, non-destructive and non-pollution [4]. Mineral infrared spectrum produced by its molecular vibration can provide large information of chemical composition and structure. MIR had been used for identifying chloritoid, but few reports about using NIR spectroscopy to test this mineral can be found. However, NIR spectroscopy is such a powerful technique and is seriously underutilized in this regard. In the present work, MIR and NIR spectroscopy have been used to analysis for structural characteristics of the mineral chloritoid. The purpose is not only to demonstrate that the NIR region provides information comparable with that obtained by MIR, but also to reveal higher sensitivity of this spectral region to structure of minerals.

Experimental methods

Materials

The sample used in this study was chloritoid collected from the argillite in the bottom of Yaopo Formation of Western Beijing. Chloritoid is in the shape of chrysanthemum-like, radial and bundle under polarized microscope. Its {001} cleavage and (010) partings are obvious, and the interference color is the first order gray under the cross-polarizer. The chemical composition of the mineral chloritoid, shown in Table 1, was analyzed by electron probe (Fig. 1 and Table 1).

MIR spectroscopy

MIR spectra were obtained in reflectance mode using a Nicolet Nexus 6700 Fourier transform infrared spectroscopy (FT-IR) spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the 4000–400 cm^{-1} range were obtained by the co-addition of 64 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.6329 cm/s . Spectra were co-added to improve the signal to noise ratio.

NIR spectroscopy

NIR spectra were collected in reflectance mode using a Nicolet Nexus FT-IR spectrometer with a Nicolet near-IR Fibreport accessory (Nicolet Nexus, Madison, Wisconsin, USA). A white light source was used, with a quartz beam splitter and TEC NIR InGaAs detector. Spectra were obtained from 10,000 to 4000 cm^{-1} (1000–2500 nm) by the co-addition of 64 scans at a resolution of 8 cm^{-1} . A mirror velocity of 1.2659 m/s was used. The spectral manipulations of baseline adjustment, smoothing and normalization were performed using the Spectra calculation software

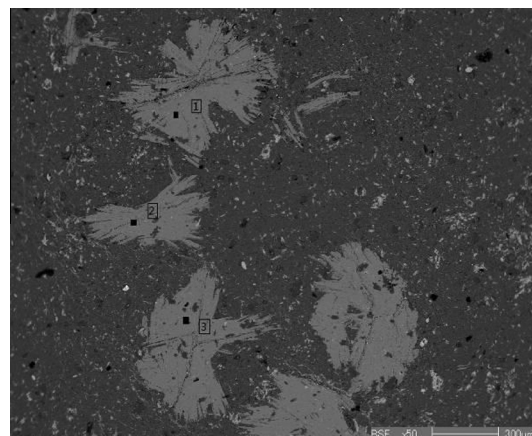


Fig. 1. Electron probe image of chloritoid.

package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was carried out using Peakfit software (Jandel Scientific, Postfach 4107, D-40688 Erkrath, Germany). Lorentz–Gauss cross product functions were used throughout and Peakfit analysis undertaken until squared correlation coefficients with $r^2 > 0.998$ were obtained.

Results and discussion

MIR spectroscopy

Chloritoid has three different layers: the Al–O layer, silicon-oxygen tetrahedral layer and brucite-type layer. And the distance between hydrogen atoms and oxygen in the trioctahedral sheet are very close to form hydrogen bonding [5]. The wavelength and shape of the absorption band associated with (OH) in many substances appear to depend on the degree of interaction between the (OH) ion and neighbor O and (OH) ions [6]. The MIR spectra of chloritoid is shown in Figs. 2 and 3. For convenience, the MIR spectra of the sample are divided into two sections; they are (a) the 3850–2850 cm^{-1} region attributed to OH stretching vibration modes (Fig. 2) and (b) the 1750–650 cm^{-1} region due to the basic aluminosilicate framework and water molecule in the structure of these two samples (Fig. 3).

3850–2850 cm^{-1} region

The infrared spectrum of chloritoid in 3850–2850 cm^{-1} region is shown in Fig. 2. Peaks present in this region are related to stretching vibrations of OH groups. The broad band at 3420 cm^{-1} support the concept of the non-equivalence of the OH units in the chloritoid structure [7]. The broad feature may be ascribed to water stretching modes; however, no water bending mode was observed in the infrared spectrum in the 1500–1800 cm^{-1} spectral range. Few reports can be found about the bands, 3675 and 3640 cm^{-1} , the former band generated by Al_2OH absorption and when a Al in the Al_2OH was displaced by Fe^{3+} (forming

Table 1
Electron probe analysis results of chloritoid ($\omega_B/\%$).

Samples	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	FeO	Total
1	0.08	0.01	39.57	25.16	0.26	0.05	0.08	0.11	0.43	28.03	93.78
2	0.08	0.00	39.36	25.08	0.05			0.15	0.58	28.66	93.96
3	0.12	0.09	40.78	25.32	0.20	0.07	0.02	0.03	0.33	26.50	93.46
Average	0.09	0.03	39.90	25.19	0.17	0.06	0.05	0.10	0.45	27.73	93.73

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