Research Article

Micro-FTIR and EPMA Characterisation of Charoite from Murun Massif (Russia)

Maria Lacalamita

Dipartimento di Scienze della Terra, Università di Pisa, 56126 Pisa, Italy

Correspondence should be addressed to Maria Lacalamita; maria.lacalamita@dst.unipi.it

Received 21 December 2017; Accepted 20 February 2018; Published 3 April 2018

Academic Editor: Javier Garcia-Guinea

Copyright © 2018 Maria Lacalamita. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Combined micro-Fourier transform infrared (micro-FTIR) and electron probe microanalyses (EPMA) were performed on a single crystal of charoite from Murun Massif (Russia) in order to get a deeper insight into the vibrational features of crystals with complex structure and chemistry. The micro-FTIR study of a single crystal of charoite was collected in the 6000–400 cm^{-1} at room temperature and after heating at 100°C. The structural complexity of this mineral is reflected by its infrared spectrum. The analysis revealed a prominent absorption in the OH stretching region as a consequence of band overlapping due to a combination of H_2O and OH stretching vibrations. Several overtones of the O-H and Si-O stretching vibration bands were observed at about 4440 and 4080 cm^{-1} such as absorption possibly due to the organic matter at about 3000–2800 cm^{-1} . No significant change due to the loss of adsorbed water was observed in the spectrum obtained after heating. The occurrence of well-resolved water bending vibration bands at about 1595 and 1667 cm^{-1} accounts for more than one structural water molecule as expected by charoite-90 polytype structure model from literature. The chemical composition of the studied crystal is close to the literature one.

1. Introduction

Charoite, $\text{K}_5\text{Ca}_8\text{Si}_{18}\text{O}_{46}(\text{OH}) \cdot n\text{H}_2\text{O}$, is a high-valued semi-precious gemstone occurring uniquely in the alkaline rocks of the Murun Massif in Yakutiya, Russia [1]. This rare silicate belongs to the group of the microporous minerals whose structure is based on a mixed tetrahedral-octahedral framework. The increased interest in these compounds came from their potential use as materials alternative to zeolites in different fields, from environmental protection to industrial applications.

The structure of charoite was only recently solved *ex novo* and “*ab initio*” in the $P2_1/m$ space group by electron diffraction data [2, 3]. Two-ordered polytypes with different cell parameters (i.e., the monoclinic “charoite-96” and orthorhombic “charoite-90”) were identified inside the sample along with other partially ordered and disordered polytypes (i.e., “charoite-2a” and “charoite-d”). The structure of both charoite-96 and charoite-90 polytypes consists of three different tubular drier silicate chains running along [001] having external and internal diameters comparable to those

of carbon nanotubes. The silicate chains are bonded by their apical oxygen to bands of edge-sharing Ca- and Na-octahedra which also run along [001] forming cavities occupied by extraframework cations (K, Sr, Ba, and Mn) and H_2O molecules. In the charoite-96, adjacent blocks of the three different chains are shifted by a translation of $1/2c$ whereas no shift occur in the charoite-90 polytype. The asymmetric unit of the charoite-90 contains 90 independent atomic positions among which three H_2O sites and one OH site partially occupied by OH^- and F^- ions [2]. For the monoclinic polytype, 87 atomic positions enclosing only one H_2O and one OH/F sites were refined [3]. A thermal study of charoite revealed that the dehydration (i.e., loss of adsorbed and structural H_2O) occurs in the temperature range 80–290°C whereas the dehydroxylation processes are observed from 290 to 480°C [4].

Apart from the detailed structural characterization, few and incomplete spectroscopic data of charoite have been reported so far in the literature. The RRUFF database contains Raman spectra collected in the range $\sim 1200\text{--}100\text{ cm}^{-1}$ whereas Buzatu and Buzgar [5] provided a wider range of

Raman signal (from ~ 4000 to 200 cm^{-1}). However, the last spectrum is characterized by strong fluorescence and noisy background which allow in distinguishing weak peaks mainly in the Si-O and Ca-O vibration region and in the position of N-H vibration (2367 , 2403 cm^{-1}) due to NH_4^+ ions which probably substitutes for K^+ in the charoite structure. No signal was observed in the OH stretching region. The infrared spectrum of charoite was reported in comparison to that of canasite in [6]. The authors observe absorption in the OH stretching and bending regions which accounts for the presence of water molecules in the charoite structure. However, no discussion or defined band assignment was reported being the structure of this mineral not yet clear at the time.

In the present study, micro-FTIR and EPMA were performed on the same single crystal in order to define the characteristic vibrational modes of charoite in the light of the recent structural determination of the mineral.

It is noteworthy that advances in the crystal chemical features of this mineral can help to determine their potential properties such as strengthening glass ceramics, ion exchange, and conductivity [7].

2. Experimental

2.1. Sample Description. Charoite occurs in charoitites of the Murun Massif (Yakutia, Russia). The Murun complex, formed at $120\text{--}150\text{ Ma}$ and covering an area of about 150 km^2 , consists of ultrapotassic aegaitic rocks with carbonates other than charoitites whose composition varies from alkaline-ultramafic to granitic [8]. Charoite crystallized jointly with other Ca-bearing alkaline minerals, such as frankamenite, canasite, miserite, tinaksite, and tokkoite [9].

The crystal studied here was handpicked under a binocular microscope starting from a fragment of asbestos-like fibers elongated along the z -axis. The selected crystal is characterized by light-violet colour and $0.10 \times 0.05 \times 0.02\text{ (mm}^3\text{)}$ dimensions.

2.2. Analytical Methods. Chemical analysis was carried out on the studied charoite crystal embedded in epoxy resin, polished and then carbon coated. The same crystal was previously subject to micro-FTIR analyses. A JEOL JXA-8200 electron microprobe operating at 15 kV accelerating voltage, 5 nA sample current, $\sim 1\text{ }\mu\text{m}$ spot size, and 40 s counting time was used. Full wavelength dispersive spectrometry (WDS) mode was employed. The used standards for major, minor, and REE components were wollastonite (Si), anorthite (Al, Ca), omphacite (Na), olivine (Mg), K-feldspar (K), Zr-jarosite (Zr), ilmenite (Ti), Cr pure (Cr), rhodonite (Mn, Zn), fayalite (Fe), celestine (Sr), sanbornite (Ba), and F-apatite (F). A Phi-Rho-Z routine was employed for the conversion from X-ray counts to oxide weight percentages (wt%). The average composition was determined over five spots.

Infrared analysis of charoite was performed at room temperature before and after heating the sample at 100°C for 4 hours. The measurements were performed on a single crystal mounted on glass capillary and laid on the cleavage plane. The spectra were collected over the range $6000\text{--}400\text{ cm}^{-1}$

using a Nicolet Avatar FTIR spectrometer with a nominal resolution of 4 cm^{-1} , equipped with a Continuum microscope, an MCT nitrogen-cooled detector, and a KBr beamsplitter. The observed IR-patterns resulted from the average of 128 scans. The OH stretching region ($3700\text{--}3000\text{ cm}^{-1}$) of the spectrum was modelled using the program *Origin Lab*, assuming Gaussian functions to describe the peaks and a linear function to approximate the background.

3. Results and Discussion

The mean weight oxides (wt%) from EPMA analysis are SiO_2 , $56.1(3)$; Al_2O_3 , $0.03(1)$; Na_2O , $3.5(3)$; MgO , $0.5(1)$; K_2O , $8.00(3)$; CaO , $20.5(6)$; TiO_2 , $0.01(3)$; Cr_2O_3 , $0.01(2)$; MnO , $1.1(1)$; FeO , $0.27(7)$; ZnO , $0.07(9)$; SrO , $0.08(4)$; ZrO_2 , $0.02(4)$; BaO , $0.12(6)$; and F, $0.1(1)$; subtotal $90.5(4)\text{ wt\%}$. The chemical formula calculated on the basis of 45 oxygen atoms is $(\text{K}_{3.31}\text{Sr}_{0.02}\text{Ba}_{0.02}\text{Mn}_{0.31}\text{Mg}_{0.24}\text{Fe}_{0.07})_{\Sigma=3.97}(\text{Ca}_{7.13}\text{Na}_{1.10})_{\Sigma=8.23}(\text{Si}_{17.99}\text{O}_{45})\text{F}_{0.10}$, compatible with the ideal chemical formula $\text{K}_5\text{Ca}_8\text{Si}_{18}\text{O}_{46}(\text{OH}) \cdot n\text{H}_2\text{O}$. It is also in good agreement with that published in [2], except for the low amount of Sr and the enrichment in Mg and Mn of the study crystal.

The typical single-crystal nonpolarized room temperature micro-FTIR spectrum of charoite in the $6000\text{--}400\text{ cm}^{-1}$ range is shown in Figure 1. The spectrum collected after heating at 100°C is illustrated in Figures 2(a) and 2(b) together with that before heating. The results of fitting of the OH stretching region of the room temperature spectrum are displayed in Figure 3 whereas the main band positions observed for the studied sample are given in Table 1. The table also contains the literature infrared and Raman data of charoite.

The spectrum in Figure 1 evidences very strong absorption bands at about $600\text{--}800\text{ cm}^{-1}$ and $\sim 1100\text{ cm}^{-1}$ which are assigned to stretching vibration of Si-O and Ca-O bonds [5, 10]. The group of bands in the $2077\text{--}1841\text{ cm}^{-1}$ range are due to the combination of Si-O absorption [11]. The most notable feature of the spectrum in Figure 1 is a very broad and intense absorption extending from ~ 3650 to 3000 cm^{-1} , peaking at $\sim 3450\text{ cm}^{-1}$, as a result of internal stretching vibration modes (ν_3 and ν_1) and bending overtone ($2\nu_2$) of water molecules overlapping with absorptions of OH groups [12]. The ν_2 bending modes are centered essentially at about 1595 and 1667 cm^{-1} (Figure 2(b), Table 1). These findings together with the absence of significant changes in the OH absorption of the heated sample (compare spectra in Figures 2(a) and 2(b)) suggest that the spectrum of the studied charoite is not affected by the contribution of the adsorbed water. In addition, the two well-resolved bands in the water bending region of the spectrum in Figure 2(b) indicate that more than one water environment occurs in the charoite structure. This feature suggests that the analysed crystal consists essentially of the orthorhombic charoite-90 polytype which contains three H_2O sites, that is, $\text{H}_2\text{O}(1)$, $\text{H}_2\text{O}(2)$, and $\text{H}_2\text{O}(3)$, other than one OH site [2]. The OH stretching region of the acquired spectrum was fitted to the smallest number of peaks needed for an accurate description of the spectral profile. The

FIGURE 1: Micro-FTIR spectrum of charoite collected at room temperature in the range 6000–400 cm⁻¹.

FIGURE 2: Micro-FTIR spectra of Figure 1 (red line) compared with that on the same crystal after heating at 100°C (green line) in the 4800–2400 cm⁻¹ region (a) and in the 2400–1400 cm⁻¹ range (b).

FIGURE 3: Decomposition of the hydrogen stretching modes region for the unheated charoite.

TABLE 1: Band position (cm^{-1}) and assignment for the bands in the infrared spectrum of the studied (see Figures 1 and 3) and literature charoite.

This study	Infrared data [6]	Raman data [5]	Band assignment
4440, 4079			—
3530, 3453, 3385, 3285, 3150	3610, 3550, 3500, 3410		OH and H ₂ O stretching
3036, 2965, 2922, 2870, 2849			C-H vibration
		2403, 2367	N-H vibration
2077, 2005, 1948, 1841			Combination of Si-O modes
1667, 1595	1650, 1620, 1590		H ₂ O bending
1508, 1458			C-H vibration
1185, 816, 759, 577		1135, 116, 1054, 675, 638, 434, 242	Si-O and M-O stretching/bending

assignment of the resulting five bands (at 3530, 3453, 3385, 3285, and 3150 cm^{-1}) is not straightforward and can be only based on chemical and structural considerations. The three H₂O molecules in the charoite-90 polytype have different local structural configurations and occupancies [2]. Specifically, the H₂O(1) molecule, located on the z -axes of the tubular chain $[\text{Si}_{12}\text{O}_{30}]^{12-}$, exhibits low occupancy (0.36) and $\langle \text{H}_2\text{O}(1)\text{-O} \rangle \geq 2.82 \text{ \AA}$; the H₂O(2) molecule occupies the large tubular chain $[\text{Si}_{17}\text{O}_{43}]^{18-}$ and shows high occupancy (0.46) and $\langle \text{H}_2\text{O}(2)\text{-O} \rangle \geq 2.97 \text{ \AA}$; the H₂O(3) molecule is instead located in a tube formed by the bent ribbon $[\text{Si}_6\text{O}_{17}]^{10-}$, two Ca-octahedra, and two Si-tetrahedra. The occupancy of the H₂O(3) site is 0.36 with $\langle \text{H}_2\text{O}(3)\text{-O} \rangle \geq 2.99 \text{ \AA}$. Generally, the shorter the H₂O-O distance, the stronger is the hydrogen bond and the lower is the frequency of the O-H stretching band [13]. Therefore, basing on the above crystal chemical considerations, the stretching vibrations of H₂O(1), H₂O(3), and H₂O(2) molecules mainly contribute to the bands at 3285, 3385, and 3453 cm^{-1} , respectively. In addition, the band at 3530 cm^{-1} can be attributed to stretching vibrations of the OH groups which substitute for the O^{2-} at the vertex of the Na-octahedra in the charoite-90 polytype. Finally, the band at 3150 cm^{-1} well corresponds to the expected position of the Fermi resonance-

enhanced overtone of the H₂O bending mode. This approach in the OH-band assignment of the FTIR spectra of minerals is well consolidated in the literature [14–16].

The obtained micro-FTIR data slightly differ from those previously found for the powder charoite [6]. Indeed, the authors identified, without a fitting analysis, four OH absorptions shifted to higher wavenumbers with respect to those here reported (see Table 1). In addition, absorption essentially centered at about 1620 cm^{-1} was generally related to water molecules with different energy [6]. This discrepancy may be ascribed to the structural complexity of this mineral which leads to the crystallization of different polytypes sometimes intimately intergrown [2].

Note also that the spectrum in Figure 1 evidences a broad band at about 3000–2800 cm^{-1} and weak bands at about 1500–1450 cm^{-1} which are typical of the C-H vibrations [17] and may be ascribed to organic matter associated to the charoite fibers. In addition, two distinctive bands appear at about 4440 and 4080 cm^{-1} whose assignment is unclear. However, their frequency is very close to the combination modes involving the fundamental stretching of OH group coupled with the Si-O stretching.

As stated above, charoite crystallized jointly with other Ca-bearing alkaline minerals whose framework is based on

various types of silicate chains. Among these minerals, the frankamenite, $K_3Na_3Ca_5[Si_{12}O_{30}](OH)F_3 \cdot H_2O$, and the miserite, $K_3Ca_{10}(Ca,M^{3+})_2[Si_{12}O_{30}][Si_2O_7]_2(O,F,OH)_2 \cdot H_2O$, are characterized by the simultaneous presence of the H_2O molecule and OH groups in the structure. Accordingly, the FTIR spectrum of frankamenite (registered with the R060100.1 code in the RRUFF database) and that of the miserite [18] exhibits two peaks centered at ~ 3600 and 3500 cm^{-1} which are, respectively, due to stretching vibrations of OH^- groups and H_2O molecules and a unique peak at the characteristic position ($\sim 1600\text{ cm}^{-1}$) of the water bending vibration. On the contrary, in canasite, $K_3Na_3Ca_5[Si_{12}O_{30}](OH,O)_{2.5}F_{1.5}$, and tokkoite, $K_2Ca_4[Si_7O_{18}(OH)](F,OH)$, the hydrogen occurs only as hydroxyl groups. This is also confirmed by the absorption at $\sim 3600\text{ cm}^{-1}$ and no signal in the water bending region of literature infrared spectra [6, 19].

Therefore, the application of the infrared spectroscopy, other than techniques such as X-ray or electron diffraction and microprobe analysis, contributes to discriminate associated minerals with similar structural framework but with different H speciation.

4. Conclusions

Micro-FTIR analysis was performed on a single crystal of charoite whose composition is similar to that reported in the literature [2]. This study contributes in updating the infrared spectroscopic database of a complex mineral specimen such as the one at hand. Indeed, the data here reported complement those previously obtained on powder charoite [6]. Decomposition of the hydrogen stretching region in several bands and analysis of the absorptions at low wavenumbers support the occurrence of OH groups and more than one H_2O molecules in the charoite structure as recently found by electron diffraction of charoite-90 polytype [2]. The not straightforward assignment of the overlapping bands in the OH stretching region is due to a combination of the O-H stretching vibration modes of hydroxyl groups and water molecules. This also reflects the structural complexity of this mineral which may crystallize in different polytypes with different hydrogen content and speciation [2].

Conflicts of Interest

The author declares that there are no conflicts of interests regarding the publication of this paper.

Acknowledgments

This work was supported by the grants from the Italian Ministry of University and Research (PRIN 2010-2011). The author thanks Professor N.V. Vladykin who donated the charoite sample studied in this work. Professor Stefano Poli is acknowledged for the facilities at the Electron Microprobe Laboratory of the Dipartimento di Scienze della Terra, Università di Milano.

References

- [1] E. I. Vorob'ev, *Charoite*, Academy Publishing 'Geo', Novosibirsk, Russia, 2008.
- [2] I. Rozhdestvenskaya, E. Mugnaioli, M. Czank et al., "The structure of charoite, $(K,Sr,Ba,Mn)_{15-16}(Ca,Na)_{32}[(Si_{70}(O,OH)_{180})](OH,F)_{4.0} \cdot nH_2O$, solved by conventional and automated electron diffraction," *Mineralogical Magazine*, vol. 74, no. 1, pp. 159–177, 2010.
- [3] I. V. Rozhdestvenskaya, E. Mugnaioli, M. Czank, W. Depmeier, U. Kolb, and S. Merlino, "Essential features of the polytypic charoite-96 structure compared to charoite-90," *Mineralogical Magazine*, vol. 75, no. 6, pp. 2833–2846, 2011.
- [4] E. Matesanz, J. Garcia-Guinea, E. Crespo-Feo, P. Lopez-Arce, F. J. Valle-Fuentes, and V. Correcher, "The high-temperature behavior of charoite," *The Canadian Mineralogist*, vol. 46, no. 5, pp. 1207–1213, 2008.
- [5] A. Buzatu and N. Buzgar, "The Raman study of single-chain silicates," in *Analele Stiintifice ale Universitatii, A. I. Cuza, Ed.*, vol. 1, Iasi, Geologie, Tomul LVI, 2010.
- [6] V. P. Rogova, Y. G. Rogov, V. A. Drits, and N. N. Kuznetsova, "Charoite, a new mineral, and a new jewelry stone," *Zapiski Vsesoyuznogo Mineralogicheskogo Obshchestva*, vol. 107, no. 1, pp. 94–100, 1978.
- [7] W. Depmeier, "From minerals to materials," in *S.V. Krivovichev: Minerals and Advanced Materials II*, Springer-Verlag, Berlin Heidelberg, 2012.
- [8] N. V. Vladykin, "Potassium alkaline lamproite-carbonatite complexes: petrology, genesis, and ore reserves," *Russian Geology and Geophysics*, vol. 50, no. 12, pp. 1119–1128, 2009.
- [9] A. A. Konev, E. I. Vorob'ev, and K. A. Lazebnik, *Mineralogy of Murunskii Alkaline Massif*, Nauchno-Izdatelsky Tsentr Ob'edinnennogo Instituta Geologii, Geofiziki, Mineralogii, Siberian Branch of Russian Academy of Science, Novosibirsk, Russia, 1996.
- [10] G. Della Ventura, F. Bellatreccia, G. C. Parodi, F. Cámara, and M. Piccinini, "Single-crystal FTIR and X-ray study of vishnevite, ideally $[Na_6(SO_4)][Na_2(H_2O)_2](Si_6Al_6O_{24})$," *American Mineralogist*, vol. 92, no. 5-6, pp. 713–721, 2007.
- [11] R. L. Frost and U. Johansson, "Combination bands in the infrared spectroscopy of kaolins—a drift spectroscopic study," *Clays and Clay Minerals*, vol. 46, no. 4, pp. 466–477, 1998.
- [12] D. Eisenberg and W. Kauzmann, *The Structure and Properties of Water*, Oxford University Press, New York, 1969.
- [13] E. Libowitzky and G. R. Rossman, "FTIR spectroscopy of lawsonite between 82 and 325 K," *American Mineralogist*, vol. 81, no. 9-10, pp. 1080–1091, 1996.
- [14] F. Scordari, E. Schingaro, G. Ventruti, M. Lacalamita, and L. Ottolini, "Red micas from basal ignimbrites of Mt. Vulture (Italy): interlayer content appraisal by a multi-methodic approach," *Physics and Chemistry of Minerals*, vol. 35, no. 3, pp. 163–174, 2008.
- [15] M. Lacalamita, E. Schingaro, F. Scordari, G. Ventruti, A. Fabbriozio, and G. Pedrazzi, "Substitution mechanisms and implications for the estimate of water fugacity for Ti-rich phlogopite from Mt. Vulture, Potenza, Italy," *American Mineralogist*, vol. 96, no. 8-9, pp. 1381–1391, 2011.
- [16] G. Ventruti, G. Della Ventura, F. Bellatreccia, M. Lacalamita, and E. Schingaro, "Hydrogen bond system and vibrational spectroscopy of the iron sulfate fibroferrite, $Fe(OH)SO_4 \cdot 5H_2O$,"

- European Journal of Mineralogy*, vol. 28, no. 5, pp. 943–952, 2016.
- [17] D. Moro, G. Valdrè, E. Mesto et al., “Hydrocarbons in phlogopite from Kasenyi kamafugitic rocks (SW Uganda): cross-correlated AFM, confocal microscopy and Raman imaging,” *Scientific Reports*, vol. 7, article 40663, 2017.
- [18] E. Kaneva, M. Lacalamita, E. Mesto, E. Schingaro, F. Scordari, and N. Vladykin, “Structure and modeling of disorder in miserite from the Murun (Russia) and Dara-i-Pioz (Tajikistan) massifs,” *Physics and Chemistry of Minerals*, vol. 41, no. 1, pp. 49–63, 2014.
- [19] N. V. Chukanov, *Infrared Spectra of Mineral Species*, Springer Geochemistry/Mineralogy, Dordrecht, 2013.