



Micro-Raman Characterization of the Lapeyreite Mineral, the Alpes-Maritimes Region, Nice, France

MURAT HATIPOGLU^{1,*} and HAKKI BABALIK²

¹Gemmology and Jewellery Programme, Izmir Multidisciplinary Vocational School, Dokuz Eylul University, TR-35380 Buca-Izmir, Turkey

²Jewellery Program, Karacasu Memnune Inci Multidisciplinary Vocational School, Adnan Menderes University, TR-09790 Karacasu-Aydin, Turkey

*Corresponding author: Tel: +90 232 3012564; E-mail: murat.hatipoglu@deu.edu.tr

(Received: 21 March 2011;

Accepted: 5 December 2011)

AJC-10798

The Raman spectroscopy is performed for the first time on the new discovered secondary copper arsenate mineral, lapeyreite $[\text{Cu}_3\text{O}[\text{AsO}_3(\text{OH})]_2 \cdot 0.75\text{H}_2\text{O}]$. The bands attributed to two main vibrating (CuO_5 and AsO_4) units are readily identified in the Raman spectrum. Symmetric stretching modes at 1047 cm^{-1} and at 627 and 405 cm^{-1} are assigned to (ν_1) CuO_5 , (ν_2) AsO_4 and (ν_3) AsO_4 units, respectively. Bending vibration modes in the Raman spectrum are assigned to (ν_2) AsO_4 units at 214 , 198 and 188 cm^{-1} and to (ν_2) CuO_5 units at 141 and 100 cm^{-1} . In addition, As-O bond and O-H-O bond lengths in the structure of lapeyreite were assigned from the FT-IR at 3420 , 2870 and 1640 cm^{-1} . The position and the intensity of both Raman vibrations reveal that the secondary occurring lapeyreite mineral is hydrothermally altered from the primary occurring cuprite mineral.

Key Words: Lapeyreite, Cuprite, Aqueous copper arsenate, Dispersive confocal micro-Raman spectroscopy, Infrared spectroscopy.

INTRODUCTION

The crystallographic-chemical investigation of the aqueous copper arsenates theoparacelsite $[\text{Cu}_3(\text{OH})_2\text{As}_2\text{O}_7]$ ¹ and lapeyreite $[\text{Cu}_3\text{O}[\text{AsO}_3(\text{OH})]_2 \cdot 0.75\text{H}_2\text{O}]$ ² has been made for last 10 years, even though yet no work based on Raman spectroscopy is reported in literatures.

Raman spectroscopy has become the principal method of non-destructive spectral analysis³ since the 1940s. Dispersive confocal micro-Raman spectroscopy (DC μ RS) is one well-known method for the characterization of minerals⁴. Therefore, the characterizations of many single minerals using Raman spectroscopy have previously been published⁵.

One of the most recently discovered minerals is lapeyreite, which has been approved as a mineral by the commission on new minerals, nomenclature and classification (CNMNC) of the International mineralogical association (IMA). Accordingly, lapeyreite is translucent dark pistachio-green and is monoclinic-prismatic, H-M symbol (2/m) and space group: C 2/m. The tenacity is brittle and the fracture conchoidal. The lattice structure of lapeyreite belongs to the group of M=M-T framework structures⁶; thus the structure is formed by a three-dimensional network of CuO_5 square pyramids and AsO_4 tetrahedra with a water molecule in a structural cavity, which contains chains of CuO_5 square pyramids and AsO_4 tetrahedra

running along the shortest cell axis² (Fig. 1). Therefore, an analysis of the Raman spectrum of lapeyreite should be possible as well as theoparacelsite in regarding with previously studies on copper formate tetrahydrate⁷. However, a comparison and contrast of the two minerals will unfortunately not be possible, since the Raman spectrum of the mineral theoparacelsite has been produced.

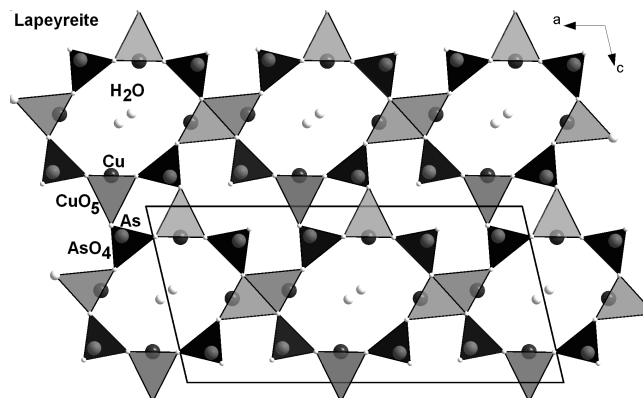


Fig. 1. Crystal structure of lapeyreite viewed along the b -axis. The CuO_5 square pyramids in light grey representing Cu in dark, AsO_4 tetrahedra in dark grey representing As in light grey. Disordered oxygen position OW7 of the water molecule shown as light spheres²

An important mineralogical feature of lapeyreite has so far remained incomplete. Therefore, this study mainly aims to present the Raman spectrum of lapeyreite and relate the spectrum to the structure of the mineral. At the same time, the paper serves to begin the systematic studies of Raman vibrational spectra of arsenate-containing aqueous copper minerals of secondary origin in the oxide supergene zone.

EXPERIMENTAL

Minerals: Holotype specimens of the mineral lapeyreite have only been deposited in three different universities in the world, as mentioned in the previously published paper². The first one is in the Laboratory of Crystallography, University of Geneva, Switzerland (registration number CR.010). The second one is in the University of Adnan Menderes, Vocational School of Memnune Inci, Karacasu-Aydin, Turkey (registration number KMY.25). The third one is in the University of Dokuz Eylül, Vocational School of Izmir, Buca-Izmir, Turkey (registration number BM.73).

The holotype specimen investigated in this study is the third one, which is currently deposited in the University of Dokuz Eylül, Vocational School of Izmir, Buca-Izmir, Turkey (registration number BM.73). Actually, all the samples were collected from the old copper mines of Roua (North and South group, municipality of Guillaumes and Daluis respectively), which are situated in the northwestern part of the Alpes-Maritimes region of France, about 50 km from Nice.

Raman microprobe spectroscopy: The crystal samples of new mineral lapeyreite were placed and oriented on the stage of an Olympus BM-41 microscope, equipped with 10x and 50x objectives and part of a Horiba Jobin Yvon Scientific XPLORA dispersive (visible) confocal micro-Raman spectrometer with a high throughput integrated spectrograph, which also includes a monochromator, a filter system and a charge-coupled device (CCD). Raman spectra were excited by a He-Ne laser (532 nm) in the range between 50 and 4000 cm^{-1} . The micro-Raman analysis was performed on a dark background at room temperature. Repeated acquisition using the highest magnification was accumulated to improve the signal-to-noise ratio. Spectra were calibrated using the 520 cm^{-1} line of a silicon wafer. Spectral manipulation as a baseline adjustment was carried out using the software of the device. Details of the technique have been published by the many authors^{3,8,9}. The Raman analysis was carried out in the Gemmological Testing Laboratory at the Izmir Multidisciplinary Vocational School of Dokuz Eylül University-Izmir (Turkey).

FT-IR spectroscopy: Fourier transform infrared absorption (FT-IR) spectrum was measured using a thermo Nicolet 6700-FTIR equipped with a CsI beam splitter and a DTGS detector. It was recorded in the spectral range of about 2900 to 4000 cm^{-1} . Spectral manipulations, such as baseline adjustment, smoothing and normalization were performed. The FT-IR analysis was carried out in the Chemistry Laboratory at the Engineering Faculty of Aegean University-Izmir (Turkey).

RESULTS AND DISCUSSION

The dispersive (visible) confocal micro-Raman spectrum in the range between 100 and 1100 cm^{-1} (Figs. 2 and 3) and

Fourier transform infrared spectrum (Fig. 4) in the range between 1100 and 4000 cm^{-1} of the new secondary mineral lapeyreite $[\text{Cu}_3\text{O}[\text{AsO}_3(\text{OH})]_2 \cdot 0.75\text{H}_2\text{O}]$ are given. In addition, the wavenumbers of these vibrational (Raman and infrared) bands and their assigned causes are given in Table-1.

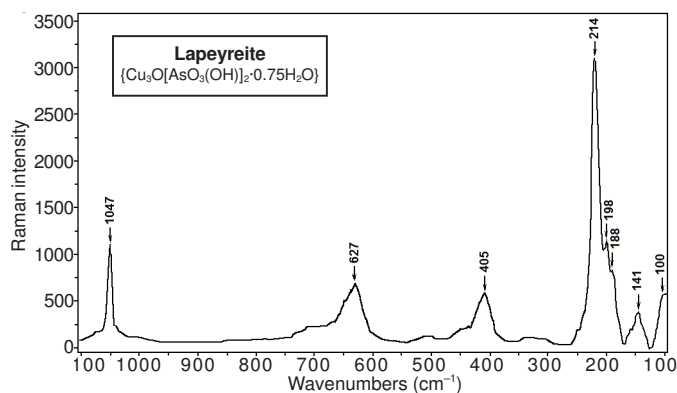


Fig. 2. Dispersive confocal micro-Raman spectrum of lapeyreite in the 100-1100 cm^{-1} region, measured at 1800T grating. No further bands were observed after the band at 1047 cm^{-1} . Therefore, the spectra were cut at the wavenumber of 1100 cm^{-1} .

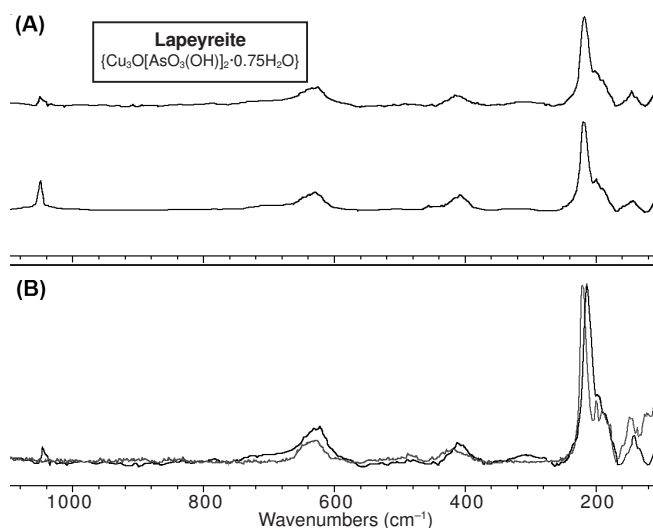


Fig. 3. Micro-Raman spectra of the mineral lapeyreite, measured at the gratings of 1200 T and 1800 T (A). The comparison and contrast of the overlapped Raman spectra of the primary mineral cuprite and the secondary mineral lapeyreite (B). The spectrum of cuprite, shown as in red line, was compiled from the library of the device

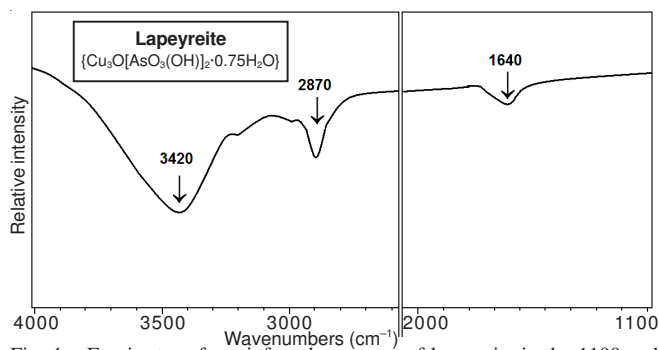


Fig. 4. Fourier transform infrared spectrum of lapeyreite in the 1100 and 4000 cm^{-1} region

It is important to note that the highly similar mineral theoparacelsite $[\text{Cu}_3(\text{OH})_2\text{As}_2\text{O}_7]$ has not yet been studied using Raman spectroscopy. Therefore, a comparison and contrast

of the micro-Raman wavenumbers of these two important arsenate-containing copper hydroxide minerals was not possible in this study. The first Raman spectroscopic data of the lapeyreite holotype sample indicate that the formation of distinctive vibrational bands is definitely related to lattice imperfections (internal defects). A total of 9 Raman bands of lapeyreite were established and their causes were attributed according to the principles of Raman stretching and bending modes^{8,9} (Table-1). Three of these bands at 1047, 141 and 100 cm^{-1} were attributed to the CuO_5 units. The others at 627, 405, 214, 198 and 188 cm^{-1} were attributed to AsO_4 units. It can be stated that the bands at 1047 and 627 cm^{-1} characterize lapeyreite and distinguish the secondary mineral lapeyreite from the primary copper mineral.

TABLE-1
DISPERSIVE CONFOCAL MICRO-RAMAN BANDS
OF LAPEYREITE SECONDARY COPPER HYDROXYL
CONTAINING ARSENATE, MINERAL AND THEIR ASSIGNED
CAUSES [THE ASSIGNMENTS WERE MODIFIED FROM THE
PRINCIPLES MENTIONED BY LEWIS AND EDWARDS⁸
AND COLOMBAN AND PRINSLOO⁹]

Micro-Raman wavenumbers (cm^{-1})	Assigned causes
1047	ν_1 Symmetric stretching modes of CuO_5 units
627	ν_2 Symmetric stretching modes of AsO_4 units
405	ν_3 Symmetric stretching modes of AsO_4 units
214	
198	ν_2 Bending modes of AsO_4 units
188	
141	
100	ν_2 Bending modes of CuO_5 units
FT-IR wavenumbers (cm^{-1})	Assigned causes
3420	
2870	(ν)OH of water stretching vibrations
1640	

An intense sharp band at 214 cm^{-1} was assigned to the ν_2 bending modes of the AsO_4 units. Another intense band at around 1047 cm^{-1} was assigned to the ν_1 symmetric stretching modes of the CuO_5 units. Empirical relations² enable the calculation of Cu-O and As-O bond lengths in lapeyreite from the observed wavenumbers and bands attributed to the ν_1 CuO_5 and ν_2 and ν_3 AsO_4 stretching vibrations (Fig. 2) (Table-1).

In addition, the intermediate wavenumber region from 250 to 100 cm^{-1} has complex vibrations. Three distinctive Raman bands were evaluated as bending modes.

No further bands were observed after the band at 1047 cm^{-1} . Therefore, the spectra were cut at the wavenumber of 1100 (Figs. 2 and 3). In fact, the vibrational stretching modes throughout the infrared region in the FT-IR spectrum of lapeyreite were obtained (Fig. 4). Therefore, IR analysis in combination with the understanding of cuprite has been used to make the proposed Raman band assignments. It is seen that As-O bond and O-H-O bond lengths in the structure of lapeyreite were assigned from the FT-infrared at 3420, 2870 and 1640 cm^{-1} .

It is stated that the lattice structure of lapeyreite belongs to the group of M=M-T framework structures⁶; thus the structure is formed by a three-dimensional network of CuO_5 square

pyramids and AsO_4 tetrahedra with a water molecule in a structural cavity which contains chains of CuO_5 square pyramids and AsO_4 tetrahedra running along the shortest cell axis². On the other hand, two H atoms compensate for the observed charge deficiency and transform one third of the O atoms O_5 and O_6 in the AsO_4 tetrahedra into OH groups¹⁰. The other two H atoms connect the water molecules in the cavity with the O atoms O_1 , O_2 , O_3 and O_4 . However, as the H atoms of two OH groups compensate for the missing positive charge at the partially occupied sites, it is possible that the protons are located inside the empty oxygen tetrahedra. The exact location of the H atoms in the structure remains to be ascertained². Slodczyk and Colomban¹¹ have stated that many electrical, electrochemical and magnetic properties result from a competition between different potentials of the chemical bonding and structure. In general, some atoms (alkali and earth alkali cations) have a strong ionic character. Some other atoms develop covalent bonding (*i.e.*, transition metals) and form strong molecular bricks. Metallic bonds can also be formed between atoms and ionized clusters between ions and complex nano-clusters may be observed¹¹.

The secondary occurring mineral lapeyreite was hydrothermally altered from primary occurring copper minerals, as was the other secondary copper mineral with arsenate content, theoparacelsite. A comparison and contrast of the overlapped Raman bands of the secondary mineral lapeyreite and the primary mineral cuprite (Fig. 3) shows that lapeyreite is definitely altered from cuprite (Cu_2O), since the Raman spectrum of cuprite is highly similar to that of lapeyreite, rather than those of the other primary copper minerals, such as calcosine, chalcopyrite, coveline and bornite. Accordingly, it can be stated that the most important band in the Raman spectrum which would be helpful to identify the mineral lapeyreite appears at 1047 cm^{-1} .

Sarp and his colleagues² stated that lapeyreite was invariably in intimate association with trippkeite and the other associated minerals were olivenite, malachite, gilmarite, cornubite, connellite, theoparacelsite, brochantite, cuprite, native copper, algononite and domeykite. In addition, lapeyreite occurred in geodes of cuprite (0.5 mm diameter) as aggregates formed from perfect elongated rectangular crystals, acicular fibrous crystals or powdery masses. In this paragenesis, the crystallization sequence of theoparacelsite¹ and lapeyreite was probably as follows: the oxidation of native copper produced cuprite; then, the reaction of copper with solutions enriched in arsenous acid produced trippkeite precipitated on the previously formed cuprite. Subsequent oxidation of arsenous acid produced arsenic acid, which also reacted with copper, yielding crystals of lapeyreite². Therefore, it can be interpreted that cuprite is primarily responsible for the occurrence of lapeyreite. In addition, Raman spectroscopy lends itself for the analysis of cuprite secondary minerals such as lapeyreite.

Conclusion

It is important to note that the dispersive confocal micro-Raman bands of the lapeyreite have not been reported in the previous literature. These first experimental data of the sample indicate that the formation of distinctive wavenumbers is definitely related to lattice defects, which can be attributed to

structural imperfections, primarily regarding a three-dimensional network of CuO₅ square pyramids and AsO₄ tetrahedra with a water molecule in a structural cavity, which contains chains of CuO₅ square pyramids and AsO₄ tetrahedra running along the shortest cell axis. Due to its similar Raman spectrum, it is claimed that the secondary mineral lapeyreite occurs from the primary copper mineral cuprite after a hydrothermal alteration.

The Raman spectrum of lapeyreite shows the most intense band at 1047 cm⁻¹ is assigned to ν_1 symmetric stretching vibration modes of CuO₅ units. The ν_2 bending modes of CuO₅ units are found at 141 and 100 cm⁻¹. The band at 627 and 420 cm⁻¹ is assigned to the ν_2 and ν_3 symmetric stretching modes of AsO₄ units, respectively. In addition, the ν_2 bending modes of AsO₄ units are found at 214, 198 and 188 cm⁻¹. On the other hand, infrared bands at 3420, 2870 and 1640 cm⁻¹ are assigned to the (ν)OH of water stretching vibrations. Since, some hydrogen bonds are present in the lapeyreite structure.

ACKNOWLEDGEMENTS

Dokuz Eylül University-Izmir is appreciated for funding the instrumentation with the grant of the BAP project, numbered BAP-2009.KB.FEN.051. The help and support during the purchasing procedure of the micro-Raman spectrometer of Prof. Dr. R. Sami AKSOY, Prof. Dr. I. Hakki BAHAR, Prof.

Dr. Can KARACA, Cengiz HEPIYILER and Prof. Dr. Necdet TÜRK are gratefully acknowledged. In addition, the authors thank the Instructor Helen Margaret MORAN-ÇAGLAR from Dokuz Eylül University, School of Foreign Languages, for proof-reading the manuscript.

REFERENCES

1. H. Sarp and R. Cerny, *Archives des Sciences Genève*, **54**, 7 (2001).
2. H. Sarp, R. Cerny, H. Babalik, M. Hatipoglu and G. Mari, *Am. Mineral.*, **95**, 171 (2010).
3. V. Deckert, M.W. George and S. Umaphy, *J. Raman Spectrosc.*, **39**, 1508 (2008).
4. A. Wang, J. Han, L. Guo, J. Yu and P. Zeng, *Appl. Spectrosc.*, **48**, 959 (1994).
5. M. Ivanda, D. Waasmaier, A. Endriss, J. Ihringer, A. Kirfel and W. Kiefer, *J. Raman Spectrosc.*, **28**, 487 (1997).
6. R.K. Eby and F.C. Hawthorne, *Acta Crystallogr. B*, **49**, 28 (1993).
7. R.P. Canterford and F. Ninio, *J. Phys. C: Solid State Phys.*, **6**, 575 (1973).
8. I.R. Lewis and H.G.M. Edwards, *Handbook of Raman Spectroscopy, From the Research Laboratory to the Process Line, Practical Spectroscopy Series*, Marcel Dekker Inc., New York (2001).
9. P. Colomban and L. Prinsloo, in eds.: J. Yatwood, R. Douthwaite and S. Duckett, *Optical Spectroscopy of Silicates and Glasses. Spectroscopic Properties of Inorganic and Organometallic Chemistry*, RSC Publishing, Vol. 40, p. 128 (2009).
10. I.D. Brown and D. Altermatt, *Acta Crystallogr. B*, **41**, 244 (1985).
11. A. Slodczyk and P. Colomban, *Materials*, **3**, 5007 (2010).