# A vibrational spectroscopic study of the copper bearing silicate mineral luddenite

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## HIGHLIGHTS

- We have studied the copper–lead silicate mineral luddenite using vibrational spectroscopy.
- This mineral is only one of many silicate minerals containing copper.
- Stretching vibrations of hydroxyl units suggest hydroxyl units exist in the structure of luddenite.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

## ABSTRACT

The molecular structure of the copper–lead silicate mineral luddenite has been analysed using vibrational spectroscopy. The mineral is only one of many silicate minerals containing copper. The intense Raman band at 978 $cm^{-1}$ is assigned to the $v_1$ ($A_{1g}$) symmetric stretching vibration of $Si_5O_{14}$ units. Raman bands at 1122, 1148 and 1160 $cm^{-1}$ are attributed to the $v_3$ $SiO_4$ antisymmetric stretching vibrations. The bands in the 678–799 $cm^{-1}$ are assigned to OSiO bending modes of the $(SiO_3)_n$ chains. Raman bands at 3317 and 3329 $cm^{-1}$ are attributed to water stretching bands. Bands at 3595 and 3629 $cm^{-1}$ are associated with the stretching vibrations of hydroxyl units suggesting that hydroxyl units exist in the structure of luddenite.

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## Introduction

The mineral luddenite is a hydrated silicate mineral of lead and copper of formula $Cu_2Pb_2Si_5O_{14} \cdot 4H_2O$ [1]. It is one of several copper silicates [2]. There are a significant number of silicate minerals which have copper as one of the main cations. These include kinoite $Ca_2Cu_2Si_3O_{10}(OH)_4$ [3], chrysocolla $(Cu,Al)_2H_2Si_2O_5(OH)_4 \cdot nH_2O$ [4,5], dioptase $CuSiO_3 \cdot H_2O$ [6], planchéite $Cu_8Si_8O_{22}(OH)_4 \cdot H_2O$ [7], shattuckite $Cu_5(SiO_3)_4(OH)_2$ [8], whelanite $Ca_5Cu_2(OH)_2CO_3$, $Si_6O_{17} \cdot 4H_2O$ [9], ajoite $(K,Na)Cu_7AlSi_9O_{24}(OH)_6 \cdot 3H_2O$ [10], apachite $Cu_9Si_{10}O_{29} \cdot 11H_2O$ [10], papagoite $CaCuAlSi_2O_6(OH)_3$ [11]. Apart from chrysocolla which appears as a normally amorphous mineral, all of these copper silicate minerals are crystalline; however the crystallinity may vary between the minerals. All of the minerals contain either hydroxy units or water units or both. These water and OH units are important for the stability of the minerals. All these minerals are of various shades of blue. This study of the mineral luddenite adds to our knowledge of silicate minerals containing copper.

Luddenite is a rare secondary mineral that forms from the oxidation of other secondary copper minerals in copper-rich

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base-metal deposits in massive fracture coatings, in vein fillings, and in vugs. It is related to other copper silicate minerals such as shattuckite. Luddenite was first found at Artillery Peak, Mohave County, Arizona, USA. Despites the type locality, only few occurrences were described in literature [12].

Luddenite is monoclinic with $a = 7.85$ Å, $b = 20.06$ Å, $c = 14.72$ Å, with $\beta = 90.78°$ and $Z = 6$ [1]. The mineral is light green in colour, sometimes said to be nickel green, and may be associated with alamosite $PbSiO_3$ [13,14] and wickenburgite $Pb_3Al[CaAlSi_{10}O_{27}(H_2O)_3]·H_2O$. The mineral is found in totally oxidised Pb–Cu sulphide ores.

The aim of this paper is to report the Raman spectra of well-defined natural luddenite mineral, and to relate the spectra of this molecule to the crystal structure. This paper follows the systematic research of the large group of oxyanion containing minerals, and especially their molecular structure using vibrational spectroscopy.

## Experimental

### Samples description and preparation

The luddenite sample studied in this work forms part of the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, Brazil, with sample code SAC-001. The mineral originated from Artillery Peak, Mohave County, Arizona, USA. The studied sample occurs in association with wickenburgite and the separation of different minerals was done with a stereomicroscope Zeiss model Stemi DV4 from the Museu de Ciência e Técnica, School of Mines of the Federal University of Ouro Preto.

### Raman microprobe spectroscopy

Crystals of luddenite were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10×, 20×, and 50× objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a CCD detector (1024 pixels). The Raman spectra were excited by a Spectra-Physics model 127 He–Ne laser producing highly polarised light at 633 nm and collected at a nominal resolution of 2 cm$^{-1}$ and a precision of ±1 cm$^{-1}$ in the range between 200 and 4000 cm$^{-1}$. Repeated acquisitions on the crystals using the highest magnification (50×) were accumulated to improve the signal to noise ratio of the spectra. Raman Spectra were calibrated using the 520.5 cm$^{-1}$ line of a silicon wafer. Clearly the crystals of luddenite are readily observed, with gem quality, making the Raman spectroscopic measurements readily obtainable.

### Infrared spectroscopy

Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the 4000–525 cm$^{-1}$ range were obtained by the co-addition of 128 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.

Spectral manipulation such as baseline correction/adjustment and smoothing were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package that enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentzian–Gaussian cross-product function with the minimum number of component

bands used for the fitting process. The Gaussian–Lorentzian ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of $r^2$ greater than 0.995.

## Results and discussion

### Vibrational spectroscopy

The Raman spectrum of luddenite over the 100–4000 cm$^{-1}$ spectral; range is reported in Fig. 1a. This figure shows the position and relative intensity of the Raman bands. It is noted that there some very low intensity bands in the OH stretching region. In order to closely identify and assign the Raman peaks, the spectrum is subdivided into sections based upon the type of vibration being analysed. The infrared spectrum of luddenite over the 500–4000 cm$^{-1}$ spectral range is reported in Fig. 1b. This spectrum displays the position and relative intensity of the infrared bands. A comparison may be made between the Raman and infrared spectra. It is note that there is significantly more intensity in the OH stretching region in the infrared spectrum. The infrared spectrum may be subdivided into subsections based upon the type of vibration being studied.

The Raman spectrum of luddenite over the 750–1200 cm$^{-1}$ spectral range is illustrated in Fig. 2a. The spectrum may be subdivided into three sections (a) Raman bands centred around 800 cm$^{-1}$, (b) the Raman band at 978 cm$^{-1}$ and (c) the series of bands at around 1150 cm$^{-1}$. The intense Raman band at 978 cm$^{-1}$ is assigned to the $\nu_1$ ($A_{1g}$) symmetric stretching vibration of $Si_5O_{14}$ units. Dowty showed that the –$SiO_3$ units had a unique band position of 980 cm$^{-1}$ [15] (see Figs. 2 and 4 of this reference). Dowty calculated the position of infrared bands for silicate structures and also showed measured spectra of the equivalent
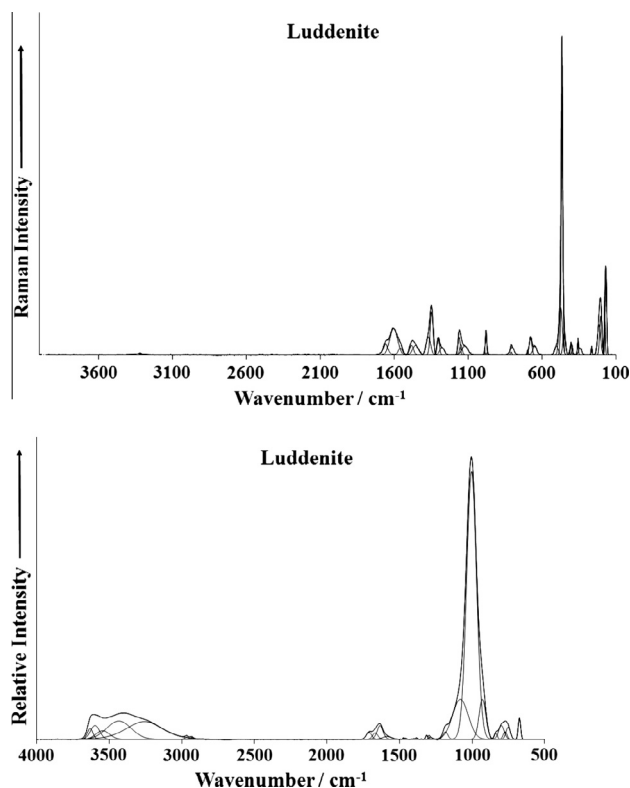


Fig. 1. (a) Raman spectrum of Luddenite (upper spectrum) and (b) infrared spectrum of Luddenite (lower spectrum).
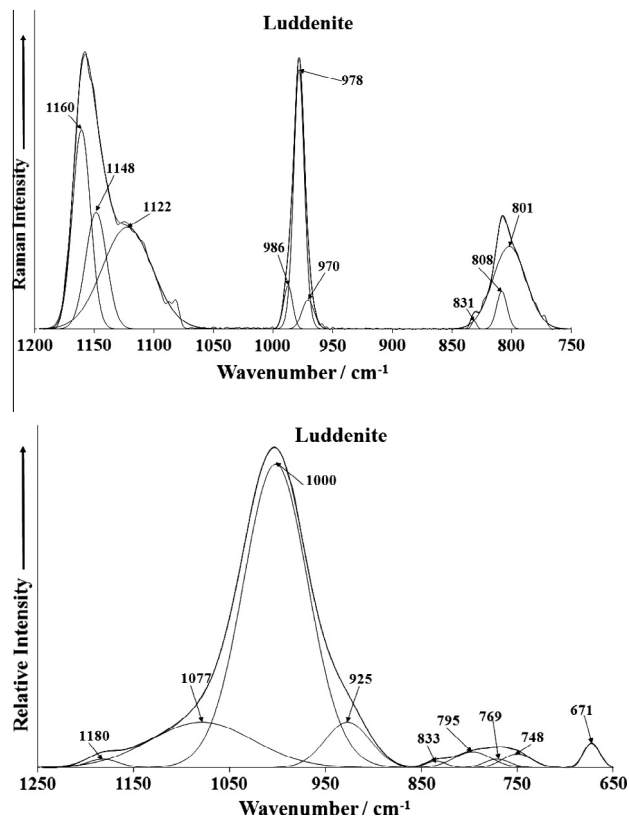
**Fig. 2.** (a) Raman spectrum of Luddenite (upper spectrum) in the 750–1200 cm$^{-1}$ spectral range and (b) infrared spectrum of Luddenite (lower spectrum) in the 650–1250 cm$^{-1}$ spectral range.
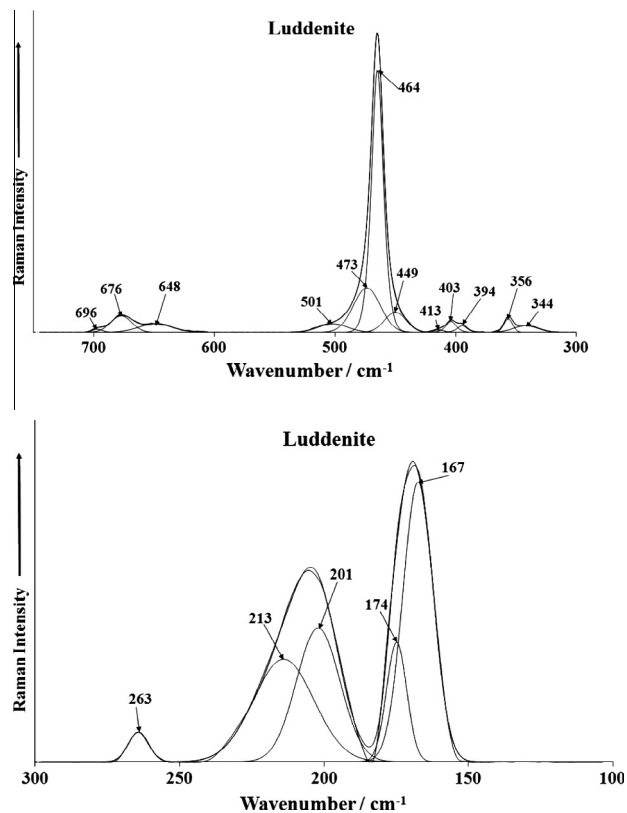


**Fig. 3.** (a) Raman spectrum of Luddenite (upper spectrum) in the 300–750 cm$^{-1}$ spectral range and (b) Raman spectrum of Luddenite (lower spectrum) in the 100–300 cm$^{-1}$ spectral range.
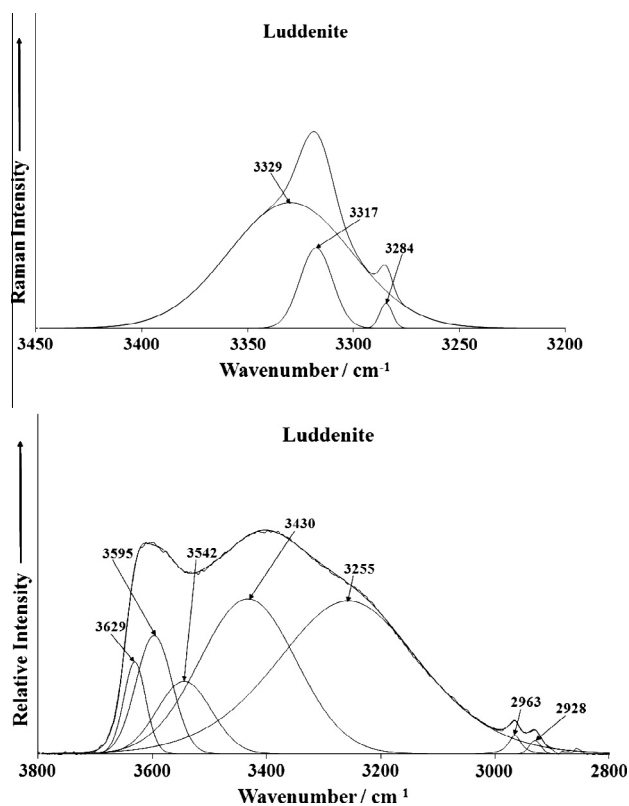


**Fig. 4.** (a) Raman spectrum of Luddenite (upper spectrum) in the 3200–3450 cm$^{-1}$ spectral range and (b) infrared spectrum of Luddenite (lower spectrum) in the 2800–3800 cm$^{-1}$ spectral range.

theoretical system. The bands in the 678–799 cm$^{-1}$ are assigned to OSiO bending modes of the (SiO$_3$)$_n$ chains. The infrared spectra as displayed by Dowty show considerable width in the peaks.

The Raman bands at 1122, 1148 and 1160 cm$^{-1}$ are attributed to the $v_3$ SiO$_4$ antisymmetric stretching vibrations. The splitting of the $v_3$ vibrational mode offers support to the concept that the SiO$_4$ tetrahedrons in luddenite are strongly distorted. The Raman band centred upon 801 cm$^{-1}$ is ascribed to water librational bands. The infrared spectrum (Fig. 2b) is dominated by a very broad band at 1000 cm$^{-1}$. Shoulder bands of this peak are found at 925, 1077 and 1180 cm$^{-1}$. In addition, some low intensity infrared bands are found at 748, 769, 795 and 833 cm$^{-1}$. In harmony with the assignment of the Raman bands in this spectral region, the bands are attributed to water librational modes.

The Raman spectra of luddenite over the 300–750 and the 100–300 cm$^{-1}$ spectral range are reported in Fig. 3. Strong Raman bands are noted at 167, 174, 201, 213 and 263 cm$^{-1}$. These bands are attributed to external vibrations. A strong Raman band at 464 cm$^{-1}$ with shoulder bands at 449, 473 and 501 cm$^{-1}$ are assigned to the SiO$_4$ $v_2$ bending mode. For a perfectly symmetric SiO$_4$ tetrahedron, only a single band at 608 cm$^{-1}$ ($A_{2u}$) should be observed. The Raman band observed at 676 cm$^{-1}$ with additional bands at 648 and 696 cm$^{-1}$ is assigned to the SiO$_4$ $v_4$ bending mode. Vedanand et al. [16] reported the $v_2$ and $v_4$ modes for stringhamite at 510 and 660 cm$^{-1}$.

The Raman spectrum of luddenite over the 3200–3450 cm$^{-1}$ spectral range is reported in Fig. 4a. This spectrum suffers from a lack of signal; nevertheless Raman bands may be resolved at 3317 and 3329 cm$^{-1}$. A shoulder band is also found at 3284 cm$^{-1}$. These bands are attributed to water stretching bands. The infrared spectrum of luddenite over the 2800–3800 cm$^{-1}$ spectral range is reported in Fig. 4b. The spectral profile is broad and
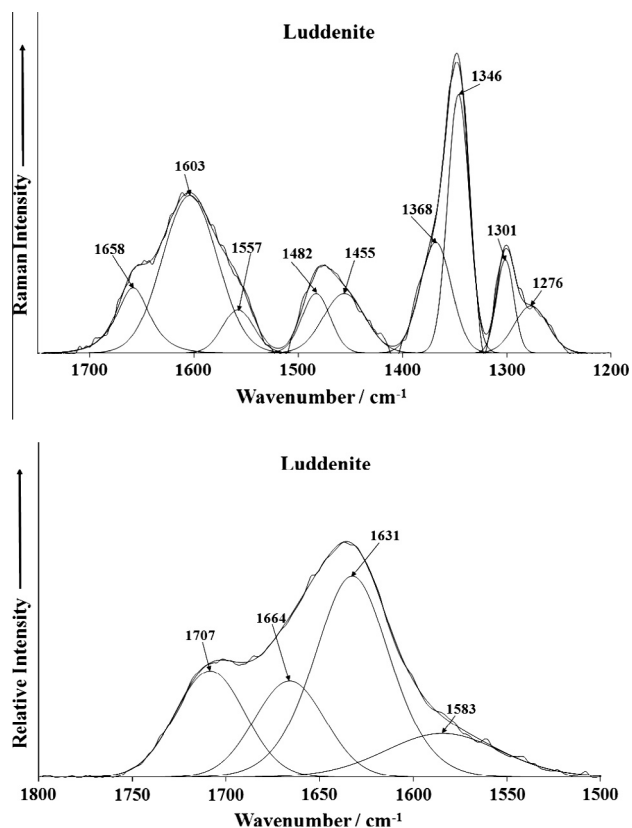
**Fig. 5.** (a) Raman spectrum of luddenite (upper spectrum) in the 1200–1750 cm$^{-1}$ spectral range (b) infrared spectrum of luddenite (lower spectrum) in the 1500–1800 cm$^{-1}$ spectral range.

infrared bands may be resolved at 3255, 3430, 3542, 3595 and 3629 cm$^{-1}$. These bands are assigned to water stretching vibrations. However, the positions of the two bands at 3595 and 3629 cm$^{-1}$ suggest that these two bands may be associated with the stretching vibrations of hydroxyl units. The two low intensity infrared bands at 2928 and 2963 cm$^{-1}$ are ascribed to organic compounds and are due to CH stretching vibrations.

The Raman spectrum of luddenite over the 1200–1800 cm$^{-1}$ spectral range is shown in Fig. 5a. The two Raman bands observed at 1603 and 1658 cm$^{-1}$ are assigned to the water bending modes. Other Raman bands are identified at 1276, 1301, 1346 and 1368 cm$^{-1}$ and are attributed to the antisymmetric stretching modes of siloxane units ($Si_5O_{14}$). Two other Raman bands are noted at 1455 and 1482 cm$^{-1}$. The Raman spectrum in this spectral region shows significantly more bands than the infrared spectrum as shown in Fig. 5b. Infrared bands are observed at 1631, 1664 and 1707 cm$^{-1}$ with a long tail centred at 1583 cm$^{-1}$. These bands are assigned to water bending modes. The observation of the three bands provides support for water existing in different molecular environments subject to different hydrogen bond strengths. The

infrared band at 1631 cm$^{-1}$ is assigned to the water bending mode of weakly hydrogen bonded water. The infrared band at 1664 cm$^{-1}$ is ascribed to water involved in strongly hydrogen bonding; whereas the band at 1707 cm$^{-1}$ is attributed to very highly strongly bonded water.

## Conclusions

The mineral luddenite is a rare mineral noted for its colour variation including an emerald green colour. The mineral has been analysed by using a combination of scanning electron microscopy with energy dispersive analysis and Raman and infrared spectroscopy. The mineral is fundamentally a silicate mineral of Cu and Pb.

Raman spectroscopy identifies stretching and bending vibrations of the $Si_2O_5$ and $Si_2O_7$ units. Raman bands attributable to trigonal boron are observed. Infrared spectra show much greater complexity making their assignment more difficult. Two Raman bands at 3547 and 3612 cm$^{-1}$ are assigned to OH stretching bands. Bands associated with water stretching vibrations are observed in the spectra of luddenite. Vibrational spectroscopy enables aspects of the molecular structure of luddenite to be ascertained.

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