

Spectroscopic analysis and X-ray diffraction of zinnwaldite

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This paper describes an X-ray diffraction and spectroscopic study, including infrared, near-infrared and Raman spectroscopy of some selected zinnwaldites. In general, zinnwaldite forms a member of the trioctahedral true micas with characteristically Li in the octahedral positions and low iron contents. Although the infrared spectrum of zinnwaldite has been described before, near infrared and Raman spectroscopy have not been used so far to study this mineral. X-ray diffraction showed that all the samples reported in this study have the 1M structure. The Raman spectra are characterised by a strong band at 700-705 cm^{-1} plus a broad band associated with the SiO modes around 1100 cm^{-1} . Less intense bands are observed around 560, 475, 403 and 305 cm^{-1} . The corresponding IR spectra show strong overlapping SiO modes around 1020 cm^{-1} plus less intense bands around 790, 745, 530, 470-475 and 440 cm^{-1} . Two overlapping OH-stretching modes can be observed around 3550-3650 cm^{-1} , in agreement with a broad band in the IR around 3450 cm^{-1} and a complex band around 3630 cm^{-1} . The near-IR spectra basically reflect combination and overtone bands associated with protons in the zinnwaldite structure. A very broad band observed around 5230 cm^{-1} is characteristic for adsorbed water while bands around 4530, 4435 and 4260 cm^{-1} can be ascribed to metal-hydroxyl groups.

1. INTRODUCTION

Zinnwaldite is a phyllosilicate of the group of the trioctahedral true micas. Its properties are similar to that of biotite, while it resembles lepidolite in its chemical aspects with high Si/Al ratio, high Li content and replacement of OH by F. In its structure it usually exhibits an ordering of the octahedral cations with Al in one of the M2 sites and Fe^{2+} , Li in the M1 and the other M2 site, causing a lowering of the symmetry of the space group from $C2/m$ to $C2$ (Rieder et al., 1996). The *1M* polytype seems to be characteristic although other polytypes are possible (Černý and Burt, 1987). Zinnwaldites are commonly found in pegmatites rich in rare elements, especially Li, where they are associated with other lithium bearing minerals such as lepidolite and spodumene. The mineral got its name from the locality Zinnwald, Erzgebirge, Saksen (nowadays known as Cínovec in the Czech Republic).

This paper describes the X-ray diffraction and spectroscopic study, including infrared, near-infrared and Raman spectroscopy of some selected zinnwaldites. Although the infrared spectrum of zinnwaldite has been described before, the near-infrared and Raman spectroscopic techniques have not been used so far to study this mineral.

2. ANALYTICAL TECHNIQUES

The XRD analyses were carried out on a Philips wide angle PW 1050/25 vertical goniometer equipped with a graphite diffracted beam monochromator. The radiation applied was $\text{CuK}\alpha$. The samples were measured at 50 % RH in stepscan mode with steps of $0.02^\circ 2\theta$.

The finely powdered samples were combined with oven dried spectroscopic grade KBr (containing approximately 1 wt% sample) and pressed into a disc under vacuum. The spectra were recorded in triplicate by accumulating 512 scans at 4 cm^{-1} resolution in the spectral range between 400 cm^{-1} and 4000 cm^{-1} using either the Perkin-Elmer 1600 series Fourier transform infrared spectrometer equipped with a LITA detector or a Nicolet Magna 750 Fourier transform infrared spectrometer equipped with a DTGS detector.

The micromount and single crystal samples were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10x, 20x, and 50x 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 resolution of 2 cm^{-1} and a precision of $\pm 1\text{ cm}^{-1}$ in the range between 200 and 4000 cm^{-1} . Repeated acquisition on the crystals using the highest magnification (50x) were accumulated to improve the signal to noise ratio in the spectra. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer.

Spectral manipulation such as baseline correction were performed using the Spectralcalc 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.

Samples used in this study were taken from the Van der Marel Collection (located at the Netherlands Institute for Sea Research (NIOZ) under curatorship of SvdG):

- 871 Zinnwald, Saksen, $(\text{K}_{0.95}\text{Na}_{0.05})\text{Li}_{0.934}(\text{Fe}^{2+})_{0.595}\text{Al}_{1.139}(\text{Si}_{3.394}\text{Al}_{0.635})\text{O}_{10}(\text{OH}_{0.617}\text{F}_{1.383})$
- 1106 Saksen, $(\text{K}_{0.92}\text{Na}_{0.07})\text{Li}_{1.04}(\text{Fe}^{2+})_{0.60}(\text{Fe}^{3+})_{0.06}\text{Mn}_{0.04}\text{Al}_{1.05}(\text{Si}_{3.26}\text{Al}_{0.74})\text{O}_{10}(\text{OH}_{0.41}\text{F}_{1.66})$
- 2012 Hoegur, Algeria, no analysis
- 2133 Tordal, Norway, no analysis, contains 1 % Sc (van der Marel and Beutelspacher, 1976)

3. RESULTS AND DISCUSSION

The XRD patterns show that three of the four zinnwaldites used in this study belong to the 1M polytype. Sample 2133 belongs to the 2M1 polytype. Sample 2012 contains an unidentified impurity with sharp peaks at 8.01, 4.616, 4.297 and 2.873 Å and two broad peaks at 4.008 and 3.028 Å (Fig. 1).

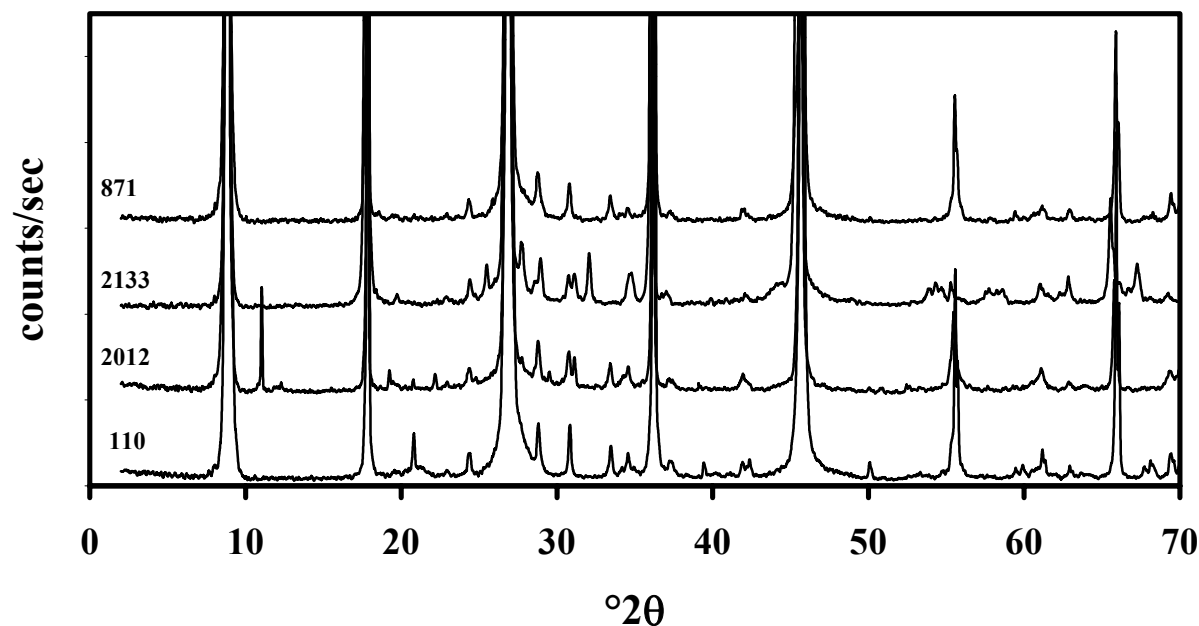


Fig. 1. XRD patterns of the zinnwaldite samples 871, 2133, 2012 and 1106.

The Raman spectra in the low wavenumber region are characterised by a strong OH-libration mode at 700-705 cm^{-1} plus a broad band associated with the SiO stretching vibrations around 1100 cm^{-1} (Fig. 2). Minor bands are observed around 560, 475, 403 and 305 cm^{-1} . The corresponding IR spectra show strong overlapping SiO modes around 1020 cm^{-1} plus less intense bands around 790, 745, 530, 470-475 and 440 cm^{-1} . Similar bands were reported by Gadsden (1975) for the infrared spectrum of zinnwaldite at 1100, 1040, 1010, 780, 740, 702, 530 and 435 cm^{-1} . The band associated with the AlO_4 unit in the tetrahedral sheet, which is coupled to the vibrations of SiO_4 , is shifted to 790 cm^{-1} due to the high amount of Fe in the structure of zinnwaldite, similar to the shift observed for ferrous phlogopites (Vedder, 1964; Farmer, 1974). The other bands below 600 cm^{-1} are probably associated with the SiO bending modes strongly coupled with vibrations of the octahedral cations, while OH-librational modes can be observed between 600 and 950 cm^{-1} (Farmer, 1974).

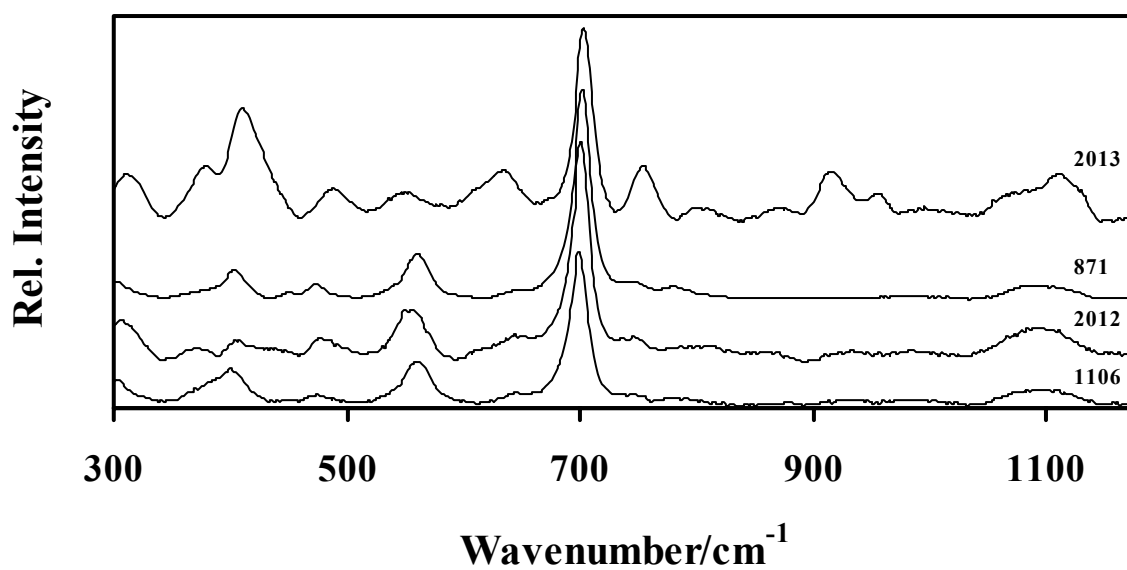


Fig. 2. Raman spectra in the region between 300 and 1175 cm⁻¹ of the zinnwaldite samples 2013, 871, 2012 and 1106.

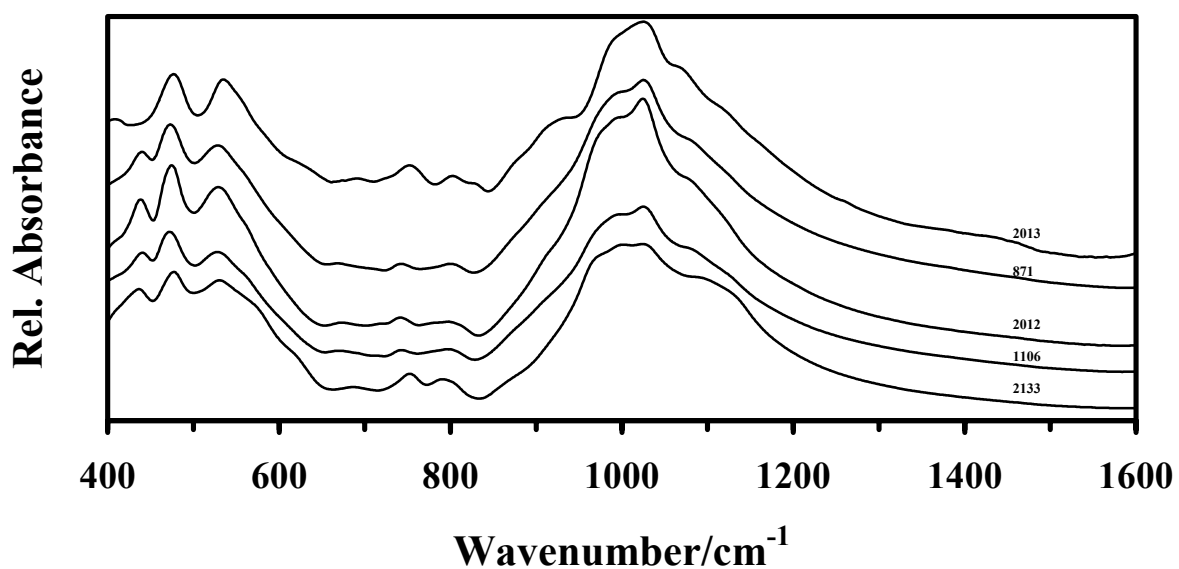


Fig. 3. FT-IR spectra in the range between 400 and 1600 cm⁻¹ of the zinnwaldite samples 2013, 871, 2012 and 1106.

The effect of Li on the OH-stretching frequencies is not well known (Farmer, 1974). For zinnwaldite two overlapping OH-stretching modes can be observed in the Raman spectra (Fig. 4) around 3550-3650 cm^{-1} , in agreement with a broad band in the IR around 3450 cm^{-1} and a complex band around 3630 cm^{-1} (Fig. 5). Gadsen (1975) reports also two bands around 3440 and 3571 cm^{-1} , while for another Li-mica, ephesite a characteristic band was observed around 3608 cm^{-1} and for Li-containing smectites a value around 3640 cm^{-1} has been found (Calvet and Prost, 1971). The differences between the zinnwaldite spectra can be explained by the substitution of the OH-groups by F.

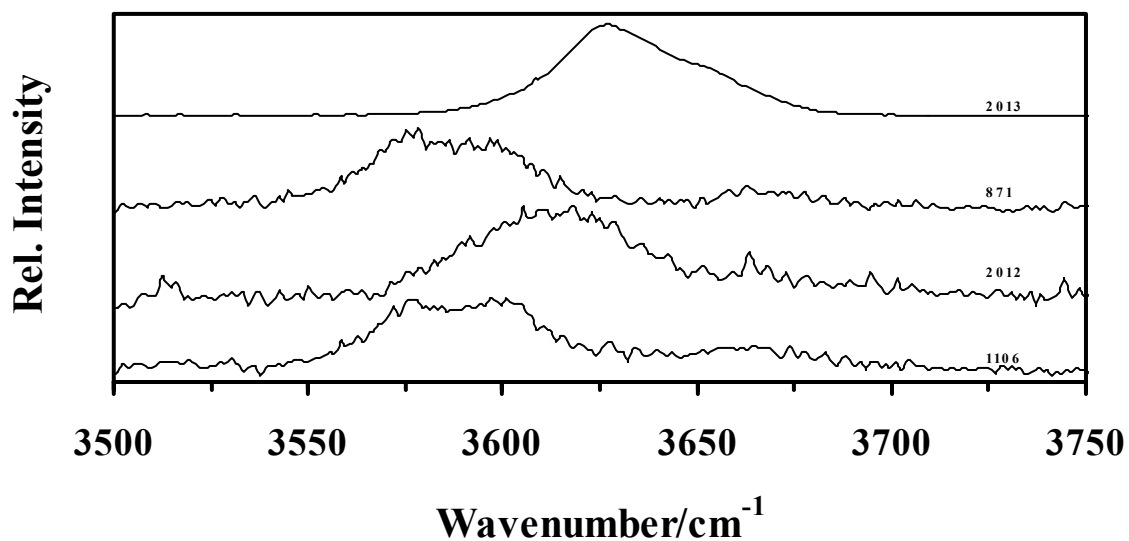
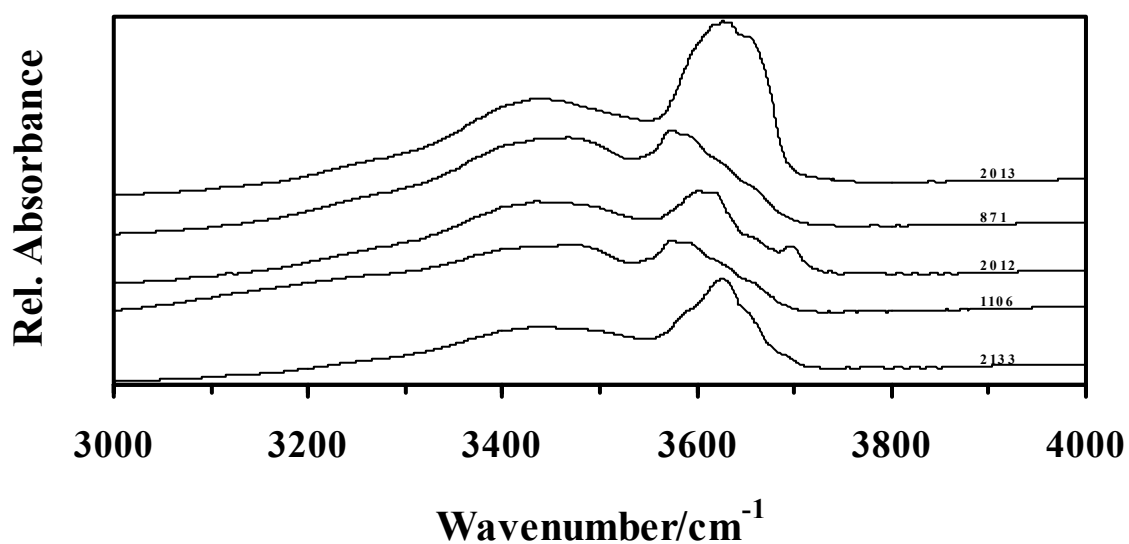


Fig. 4 and 5. Raman (top) and FT-IR (bottom) spectra in the range between 3500 and 3750 cm^{-1} of the zinnwaldite samples 2013, 871, 2012 and 1106.



The near-IR spectra basically reflect combination and overtone bands associated with protons in the zinnwaldite structure. Characteristic are a very broad band around 5230 cm^{-1} characteristic for adsorbed water plus bands around 4530, 4435 and 4260 cm^{-1} that can be ascribed to metal-hydroxyl groups (Kloprogge et al., 2000).

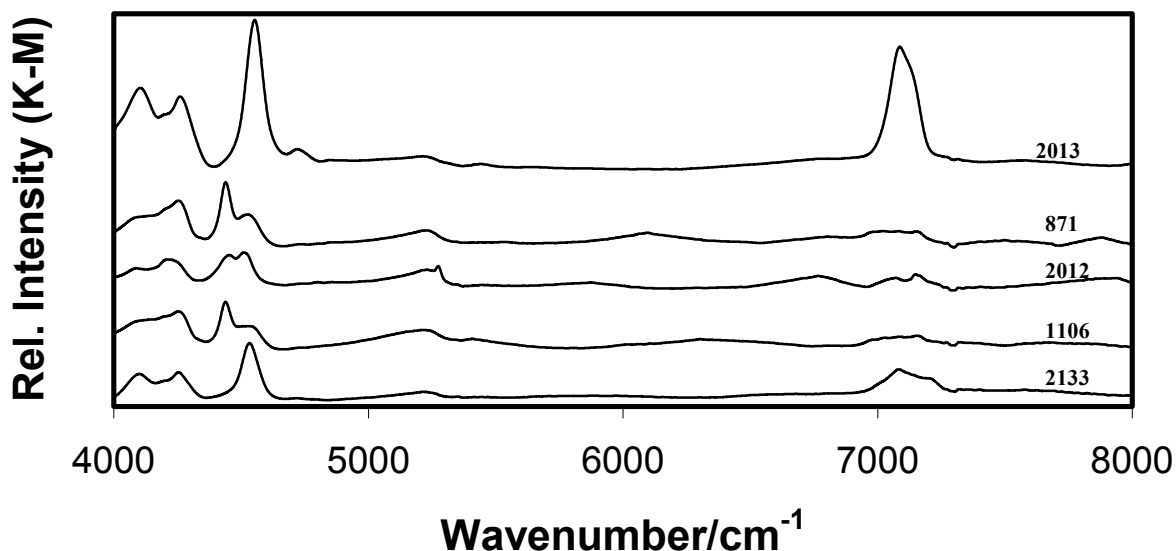


Fig. 6. Near-IR spectra in the range from 4000 to 8000 cm^{-1} of the zinnwaldite samples 2013, 871, 2012, 1106 and 2133.

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