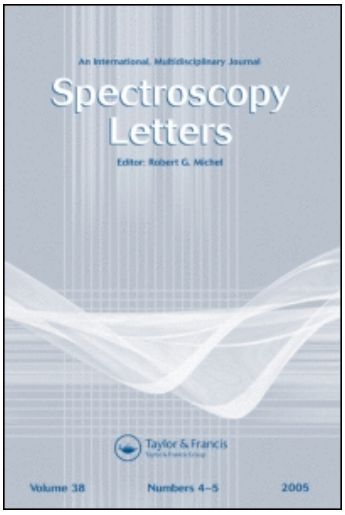

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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Ray L. Frost[a]; Silmarilly Bahfenne[a]
[a] Chemistry Discipline, Faculty of Science and Technology, Queensland University of Technology, Brisbane Queensland, Australia

Online publication date: 11 January 2011

To cite this Article Frost, Ray L. and Bahfenne, Silmarilly(2011) 'Raman Spectroscopic Study of the Mineral Thorikosite $Pb_3(OH)(SbO_3,AsO_3)Cl_2$: A Mineral of Archaeological Significance', Spectroscopy Letters, 44: 1, 63 — 66
To link to this Article: DOI: 10.1080/00387010903508580
URL: http://dx.doi.org/10.1080/00387010903508580

Spectroscopy Letters, 44:63–66, 2011

ISSN: 0038-7010 print/1532-2289 online
DOI: 10.1080/00387010903508580

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Raman Spectroscopic Study of the Mineral Thorikosite $Pb_3(OH)(SbO_3,AsO_3)Cl_2$: A Mineral of Archaeological Significance

Ray L. Frost, and Silmarilly Bahfenne

Chemistry Discipline, Faculty of Science and Technology, Queensland University of Technology, Brisbane Queensland, Australia

ABSTRACT The mineral thorikosite $Pb_3(OH)(SbO_3,AsO_3)Cl_2$ is named after the ancient city of Thorikos, in the region of Attica, where the ancient mine sites dating back to the bronze ages are found. Raman spectra of the antimonite-bearing mineral thorikosite $Pb_3(OH)(SbO_3,AsO_3)Cl_2$ were studied and were related to the structure of the mineral. Two intense Raman peaks were observed at 596 and 730 cm^{-1} and were assigned to the $Sb^{3+}O_3$ and $As^{3+}O_3$ stretching vibrations. A peak at 1085 cm^{-1} is assigned to the $Sb^{3+}OH$ deformation mode. Raman band at 325 cm^{-1} is assigned to an OAsO bending vibration of the $As^{3+}O_3$ units, and the bands at 269 and 275 cm^{-1} are attributed to the OSbO bending modes of the $Sb^{3+}O_3$ units. The intense Raman bands at 112 and 133 cm^{-1} are associated with PbCl stretching modes. Minerals such as nealite and thorikosite are minerals of archaeological significance. Yet no spectroscopic studies of these minerals had been undertaken.

KEYWORDS antimonite, archaeology, coquandite, nealite, Raman spectroscopy, thorikosite

INTRODUCTION

The mineral thorikosite $Pb_3(OH)(SbO_3,AsO_3)Cl_2$[1] is named after the ancient city of Thorikos, in the region of Attica, where the ancient mine sites dating back to the bronze ages are found.[2–4] Thorikosite is a naturally occurring member of the bismuth oxyhalide group and is isostructural with $LiBi_3O_4Cl_2$.[1] The mineral belongs to the crystal system Tetragonal–Ditetragonal Dipyramidal, H-M symbol (4/m 2/m 2/m) and space group I 4/mmm.[1] Thorikosite is tetragonal, with space group l4fmnut, with a = 3.919(l), c = 12.85a\il4, v = 197.4(l)A3a, and Z = 1. There are two crystallographic distinct Pb cations with different coordinations. Pb1 has eightfold-coordination with ligands of 4 Cl atoms, 4 O atoms, and one stereoactive lone-pair, whereas Pb2 has ninefold-coordination with ligands of 4 Cl atoms and 5 O atoms. The mineral is a pseudomineral as it is basically man-made through the reaction of sea water with lead-bearing slags. The mineral is similar to other pseudominerals such as nealite $Pb_4Fe^{2+}(AsO_3)_2Cl_4 \cdot 2H_2O$.

Received 8 November 2009; accepted 24 November 2009.

Address correspondence to Ray L. Frost, Chemistry Discipline, Faculty of Science and Technology, Queensland University of Technology, GPO Box 2434, Brisbane Queensland 4001, Australia. E-mail: r.frost@qut.edu.au

Thorikosite is found associated with lyarocerussite, paralaurionite, sphalerite, and calcite in the slags of Laurion, Greece. The minerals are found in the ancient slags that were dumped into coves and bays along the Greek coast between about 3,000 BC and 200 BC. Minerals such as nealite and thorikosite are minerals of archaeological significance. Yet no spectroscopic studies of these minerals had been undertaken.

It is interesting that very few papers have been published on the spectroscopy of antimonite and arsenite minerals. What research has been published is related to the analysis of pigments.[5–7] Very few studies of related minerals such as mineral antimonites and arsenites have been undertaken using vibrational spectroscopy,[8–10] even though Raman spectroscopy has proven especially useful for the study of minerals. To the best of the authors' knowledge, the Raman spectrum of thorikosite has not been published. The aim of this paper is to report the Raman spectra of thorikosite and to relate the spectra to the chemistry of the mineral. This paper follows the systematic research on Raman and infrared spectroscopy of secondary minerals containing oxyanions formed in the oxidation zone of minerals.

MATERIALS AND METHODS

Minerals

The mineral thorikosite was obtained from the Mineralogical Research Company . The mineral originated from Laurium, Greece. The composition of the mineral has been published.[11]

Raman Spectroscopy

Crystals of thorikosite 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 polarized 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 100 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. Alignment of all crystals in a similar orientation was attempted and achieved. However, differences in intensity may be observed due to minor differences in the crystal orientation.

Band component analysis was undertaken using the Jandel Peakfit (Erkrath, Germany) software package, which enabled the type of fitting function to be selected and allowed specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentz-Gauss cross-product function with the minimum number of component bands used for the fitting process. The Lorentz-Gauss ratio was maintained at values greater than 0.7, and fitting was undertaken until reproducible results were obtained with squared correlations (r^2) greater than 0.995. Band fitting of the spectra is quite reliable providing there is some band separation or changes in the spectral profile.

RESULTS AND DISCUSSION

The Raman spectrum of thorikosite over the full wave-number range is displayed in Fig. 1. This figure shows the relative intensity and position of the peaks. It is noted that no Raman bands are to be found in the 1100–3100 cm^{-1} region. The Raman spectrum in the 400–1100 cm^{-1} region is displayed in Fig. 2. Two intense Raman peaks are observed at 596 and 730 cm^{-1} and are assigned to the $Sb^{3+}O_3$ and $As^{3+}O_3$ stretching vibrations. A low intensity band is observed at 657 cm^{-1}. This band may be due to the stretching modes of the mixed species

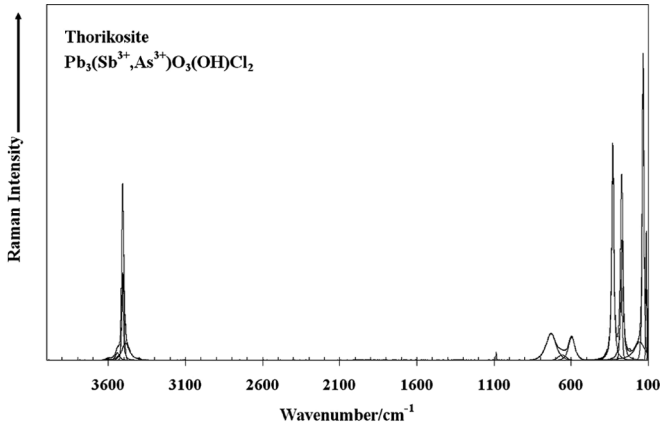

FIGURE 1 Raman spectrum of thorikosite over the complete wave-number range.

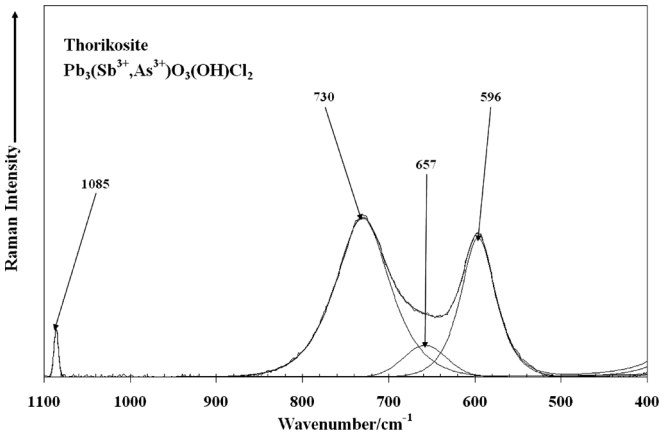

FIGURE 2 **Raman spectrum of thorikosite in the 400–1100 cm^{-1} range.**

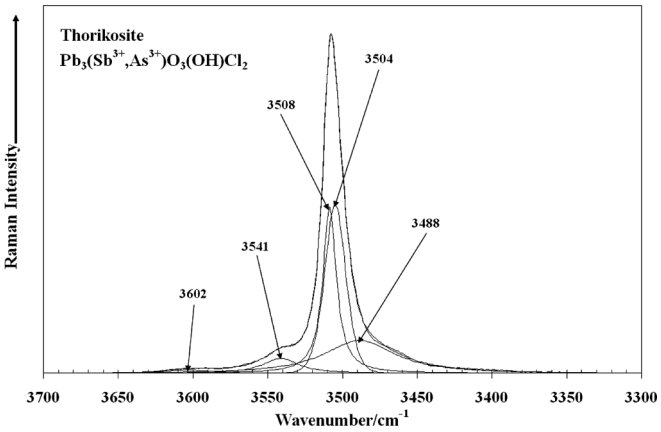

FIGURE 4 **Raman spectrum of thorikosite in the 3300–3700 cm^{-1} range.**

$(Sb,As)O_3$. The peak at 1085 cm^{-1} is thought to be due to the $Sb^{3+}OH$ deformation mode. An alternative explanation rests with the attribution to a carbonate impurity in the mineral. The low wave-number region is displayed in the 100–400 cm^{-1} region in Fig. 3. Prominent bands are observed at 269, 275, and 325 cm^{-1}. The Raman band at 325 cm^{-1} is assigned to an OAsO bending vibration of the $As^{3+}O_3$ units, and the bands at 269 and 275 cm^{-1} are attributed to the OSbO bending modes of the $Sb^{3+}O_3$ units. The AsO_3 and SbO_3 units occupy the same sites in the mineral structure; however, this will not affect the bending modes. The intense Raman bands at 112 and 133 cm^{-1} are associated with PbCl stretching modes.

The Raman spectrum of thorikosite in the 3300–3700 cm^{-1} region is shown in Fig. 4. We observed at 3506 cm^{-1} an intense band that was asymmetric and had shoulder bands at 3488, 3541 and a low intensity band at 3602 cm^{-1}. It is likely that coupling effects are observed as evidenced by the number of low-intensity bands in this spectral region. The broad feature at 3488 cm^{-1} is attributed to water OH stretching vibrations. The water may be adsorbed on the surface of the mineral, or alternatively water may be involved in the thorikosite structure. The Raman band at 3541 cm^{-1} is assigned to water adsorbed on the mineral surface. The two bands at 3504 and 3508 cm^{-1} are attributed to the OH stretching vibration of hydroxyl units. The Raman band at 3602 cm^{-1} is ascribed to an impurity.

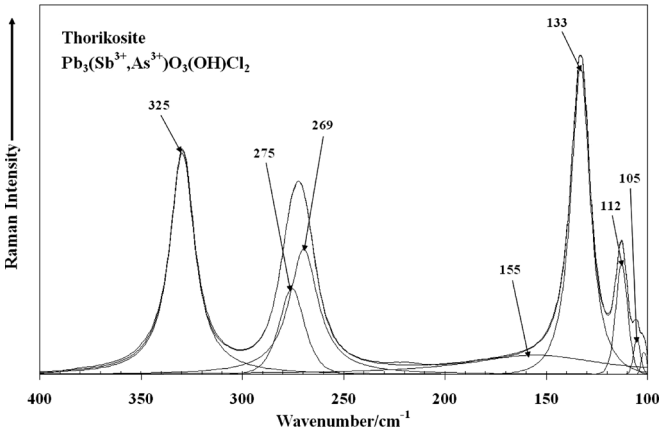

FIGURE 3 **Raman spectrum of thorikosite in the 100–400 cm^{-1} range.**

CONCLUSIONS

The mineral thorikosite $Pb_3(OH)(SbO_3,AsO_3)Cl_2$ is named after the ancient city of Thorikos, in the region of Attica, where the ancient mine sites dating back to the bronze ages are found. The mineral is a pseudomineral as it is basically man-made through the reaction of sea water with lead-bearing slags. Two intense Raman peaks are observed at 596 and 730 cm^{-1} and are assigned to the $Sb^{3+}O_3$ and $As^{3+}O_3$ stretching vibrations. A peak at 1085 cm^{-1} is assigned to the $Sb^{3+}OH$ deformation mode. A Raman band at 325 cm^{-1} is assigned to an OAsO bending vibration of the $As^{3+}O_3$ units, and the bands at 269 and 275 cm^{-1} are attributed to the OSbO bending modes of the $Sb^{3+}O_3$ units.

ACKNOWLEDGMENTS

The authors are grateful for the financial and infrastructure support of the Queensland University of

Technology Chemistry Discipline, Faculty of Science and Technology. The authors thank the Australian Research Council (ARC) for funding the instrumentation.

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