Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 125 (2014) 313–318

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

A vibrational spectroscopic study of the arsenate minerals cobaltkoritnigite and koritnigite

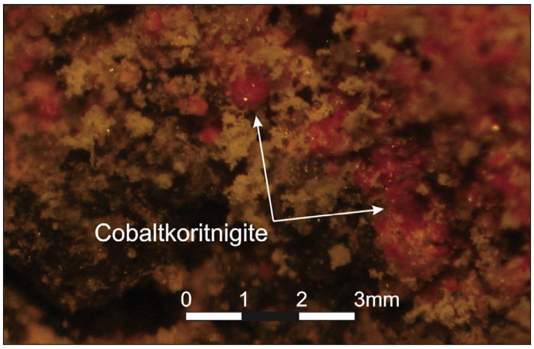
Ray L. Frost [a,*], Andrés López [a], Yunfei Xi [a], Cristiano Lana [b], Larissa Souza [c], Ricardo Scholz [b], Jiří Sejkora [d], Jiří Čejka [a,d]

[a] School of Chemistry, Physics and Mechanical Engineering, Science and Engineering Faculty, Queensland University of Technology, GPO Box 2434, Brisbane, Queensland 4001, Australia
[b] Geology Department, School of Mines, Federal University of Ouro Preto, Campus Morro do Cruzeiro, Ouro Preto, MG 35400-00, Brazil
[c] Mining Engineering Department, School of Mines, Federal University of Ouro Preto, Campus Morro do Cruzeiro, Ouro Preto, MG 35400-00, Brazil
[d] Department of Mineralogy and Petrology, National Museum, Cirkusová 1740, CZ-193 00, Praha 9, Czech Republic

HIGHLIGHTS

- Raman and infrared spectra of cobaltkoritnigite were obtained and interpreted.
- A comparison is made with koritnigite.
- Some phosphate substitution is observed.
- Raman bands were attributed to the $(AsO_3OH)^{2-}$ stretching and bending vibrations.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 27 November 2013
Received in revised form 19 January 2014
Accepted 22 January 2014
Available online 6 February 2014

Keywords:
Cobaltkoritnigite
Koritnigite
Hydrogen-arsenate
Raman spectroscopy
Molecular water
Hydrogen bonds

ABSTRACT

Raman spectra of two well-defined types of cobaltkoritnigite and koritnigite crystals were recorded and interpreted. Significant differences in the Raman spectra of cobaltkoritnigite and koritnigite were observed. Observed Raman bands were attributed to the $(AsO_3OH)^{2-}$ stretching and bending vibrations, stretching and bending vibrations of water molecules and hydroxyl ions. Both Raman and infrared spectra of cobaltkoritnigite identify bands which are attributable to phosphate and hydrogen phosphate anions proving some substitution of phosphate for arsenate in the structure of cobaltkoritnigite. The O—H···O hydrogen bond lengths in the crystal structure of koritnigite were inferred from the Raman spectra and compared with those derived from the X-ray single crystal refinement. The presence of $(AsO_3OH)^{2-}$ units in the crystal structure of cobaltkoritnigite and koritnigite was proved from the Raman spectra which supports the conclusions of the X-ray structure analysis.

Introduction

Cobaltkoritnigite is the Co member of the koritnigite group that also includes magnesiokoritnigite, the Mg member. Cobaltkoritnigite was first described from Schwarzenberg District, Saxony, Germany [1]. The mineral crystallizes with triclinic symmetry, space group *P*-1, unit cell paramethers $a = 7.95$ Å, $b = 15.83$ Å, $c = 6.67$ Å, $\alpha = 90.9°$, $\beta = 96.6°$, $\gamma = 90.0°$. Despite the type locality, a number of occurrences are reported in the literature [2–4]. A recent study of the structure of the mineral koritnigite has been published [5]. In this work we make a comparison between the Raman spectra of cobaltkoritnigite and koritnigite and an assessment of their molecular structures.

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[*] Corresponding author. Tel.: +61 7 3138 2407; fax: +61 7 3138 1804.
E-mail address: r.frost@qut.edu.au (R.L. Frost).

http://dx.doi.org/10.1016/j.saa.2014.01.106
1386-1425/

The Raman spectra of the tetrahedral anions in aqueous systems are well known. The symmetric stretching vibration of the arsenate anion (ν_1) is observed at 810 cm^{-1} and coincides with the position of the asymmetric stretching mode (ν_3) [6–8]. The symmetric bending mode (ν_2) is observed at 342 cm^{-1} and the out-of-plane bending modes (ν_4) is observed at 398 cm^{-1}. Of all the tetrahedral oxyanions spectra, the positions of the arsenate vibrations occur at lower wavenumbers than any of the other naturally occurring mineral oxyanions spectra. Farmer lists a number of spectra of arsenates including the basic copper arsenates olivenite and euchroite [9]. The effect of the arsenate ion in a crystal will be to remove the degeneracy and allow splitting of the bands according to factor group analysis. The ν_1 and ν_3 bands of olivenite and euchroite were observed at 860, 828, 790 cm^{-1} and 830 and 770 cm^{-1} respectively. The bending modes were found at 493 and 452 cm^{-1} for olivenite and at 475 and 410 cm^{-1} for euchroite.

Complex solution chemistry involving mixtures of the cations of lead, zinc, and ferric iron results in the formation of the koritnigite group of minerals, including cobaltkoritnigite. The type of mineral formed is a function of concentration, pH, temperature and the available anion present in the mother solution. The complex set of variable requires a multidimensional phase diagram [10]. Raman spectroscopy has proven an excellent technique for the study of oxyanions in both solution and in secondary mineral formation. In this work we extend our studies to the arsenates of the koritnigite mineral group. The aim of this paper is to report the Raman spectra of cobaltkoritnigite, and to relate the spectra to the molecular structure of this hydrogen-arsenate mineral. A comparison is made with the spectra of koritnigite. The paper follows the systematic research of the large group of supergene minerals and especially molecular structure of minerals containing oxyanions using IR and Raman spectroscopy.

Experimental

Samples description and preparation

The cobaltkoritnigite 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-120. The sample is from Richelsdorf District, Hessen, Germany and occurs as spheric to radiating aggregates up to 1 mm. The studied sample of the mineral koritnigite was found in the Jáchymov ore district, the Krušné hory Mountains, Western Bohemia, Czech Republic and is characterized by strawberry pink to pale purple individual crystals formed radiating aggregates up to 1 mm across. Details of the chemical analysis of this mineral have been published [5].

The sample was gently crushed and the associated minerals were removed under a stereomicroscope Leica MZ4. Scanning electron microscopy (SEM) in the EDS mode was applied to support the mineral characterization.

Scanning electron microscopy (SEM)

Experiments and analyses involving electron microscopy were performed in the Center of Microscopy of the Universidade Federal de Minas Gerais, Belo Horizonte, Minas Gerais, Brazil (http://www.microscopia.ufmg.br). Cobaltkoritnigite crystals were analysed with 5 μm coating of carbon. Secondary Electron and Backscattering Electron images were obtained using a JEOL JSM-6360LV equipment. Qualitative and semi-quantitative chemical analyses in the EDS mode were performed with a ThermoNORAN spectrometer model Quest and were applied to support the mineral characterization.

Raman microprobe spectroscopy

Crystals of cobaltkoritnigite or koritnigite 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.

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

Chemical characterization

The BSI image of cobaltkoritnigite sample studied in this work is shown in Fig. S1. The image shows a 50 μm aggregate of platy crystals. Fragments up to 2 μm of an unidentified Al sulphate occur in association. Qualitative and semi-quantitative chemical composition shows a Co arsenate with minor amounts of Al. The chemical analysis is reported in Fig. S2.

Vibrational spectroscopy background

The basis of the interpretation of the spectra of both Raman and infrared spectroscopy are given in detail in Ref. [5] and is in part repeated here. Farmer [9] presented and interpreted the mainly infrared spectra of many arsenate minerals (chapter 17). In this chapter discussion of the vibrational spectra of phosphates and arsenates is provided. The spectra of koritnigite and cobaltkoritnigite was not found. According to Myneni et al. [11,12] and Nakamoto [13], $(AsO_4)^{3-}$ is a tetrahedral unit, which exhibits four fundamental vibrations: the Raman active ν_1 symmetric stretching vibration (A_1) at 818 cm^{-1}; the Raman active doubly degenerate ν_2 symmetric bending vibration (E) observed at 350 cm^{-1}, the infrared and Raman active triply degenerate ν_3 antisymmetric stretching vibration (F_2) found around 786 cm^{-1}, and the infrared and Raman active triply degenerate ν_4 bending vibration (F_2) observed at 405 cm^{-1}. Protonation, metal complexation, and/or adsorption