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ScienceDirect

Polyhedron 26 (2007) 4503–4508

POLYHEDRON

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Hydrated double carbonates – A Raman and infrared spectroscopic study

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Received 30 April 2007; accepted 2 June 2007
Available online 12 June 2007

Abstract

The Raman spectra of selected double carbonates including pirssonite, gaylussite, shortite and quintinite complemented with infrared spectra have been used to characterise the structure of these carbonate minerals. By using a Libowitzky type function hydrogen bond distances for these minerals of 2.669–2.766 Å are estimated. The variation in the hydrogen bond distances contributed to the stability of the mineral. The Raman spectrum of pirssonite shows a single band at 1080 cm^{-1} attributed to the $(CO_3)^{2-}$ symmetric stretching mode, in contrast to shortite and quintinite where two bands are observed. Multiple bands are observed for the antisymmetric stretching and bending region for these minerals proving that the carbonate unit is distorted in the structure of pirssonite and gaylussite.

Keywords: Hydrated carbonates; Smithsonite; Pirssonite; Gaylussite; Tunisite; Shortite; Infrared and Raman spectroscopy

1. Introduction

In nature there exists a number of hydrated double carbonates including pirssonite $Na_2CO_3 \cdot CaCO_3 \cdot 2H_2O$ of space group *Fdd*2 and symmetry C_{2v}, gaylussite $Na_2CO_3 \cdot CaCO_3 \cdot 5H_2O$ of space group *C*2/*c* and symmetry C_{2h}, dawsonite $NaAl(CO_3)(OH)_2$ of space group *Ima*2 and symmetry C_{2v} and tunisite $NaHCa_2Al_4(CO_3)_4(OH)_{10}$ of space group *P*4/*nmm* and symmetry D_{4h} [1]. Pirssonite is one of several carbonate minerals that form in non-marine evaporite deposits. Other evaporite carbonates include trona, gaylussite, northupite, nahcolite and thermonatrite. Evaporite minerals are geologically important since these minerals clearly relate to the environmental conditions that existed at the time of their deposition, usually arid. Pirssonite and gaylussite differ only in the number of water molecules, yet their symmetries are quite different [2–6]. This is an indication of a change in their respective crystal structures. The two are best distinguished by their crystal habits in which pirssonite has a distinctive tabular diamond-shaped crystal form.

The infrared spectra of these double carbonates have been published [7–9]. Adler and Kerr predicted, based upon the infrared spectra, that all of the carbonate units in the crystal structure or pirsonnite and gaylussite were equivalent [8]. Farmer states that the carbonate ion in gaylussite is on a site with C_1 point symmetry. The carbonate ion is regular with bond lengths between 1.280 and 1.290 Å which implies very little distortion of the carbonate ion. Adler and Kerr reported infrared bands of pirssonite at 1068 cm^{-1} (ν_1), 870 cm^{-1} (ν_2), 1414 and 1488 cm^{-1} (ν_3), 699 and 712 cm^{-1} (ν_4) [8]. In contrast, the carbonate ion in pirssonite is highly distorted and CO bond lengths vary from 1.281 to 1.300 Å. This distortion manifests itself in the infrared spectra where splitting of the ν_2 and ν_4 modes occurs [1]. Adler and Kerr reported infrared bands of gaylussite at 875 cm^{-1} (ν_2), 1414 cm^{-1} (ν_3), 692 and 720 cm^{-1} (ν_4) [8]. The position of the symmetric stretching mode of gaylussite was not published. In contrast the infrared spectrum of gaylussite shows no intensity in the ν_1 position and

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0277-5387/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2007.06.003

no splitting of the ν_3 mode. Johan et al. published the position of the infrared bands of tunisite at 1155 cm^{-1} (ν_1), 850 cm^{-1} (ν_2), 1530 cm^{-1} (ν_3) [7]. No band position was given for the (ν_4) mode. For these minerals the position as determined by infrared spectroscopy of the water bands was not forthcoming.

Raman spectroscopy has proven very useful for the study of minerals [10–12]. Indeed Raman spectroscopy has proven most useful for the study of diagentically related minerals as often occurs with carbonate minerals [13–17]. Some previous studies have been undertaken by the authors using Raman spectroscopy to study complex secondary minerals formed by crystallisation from concentrated sulfate solutions [18]. Very few spectroscopic studies of the hydrated double carbonates have been forthcoming and what studies that are available are not new. Few Raman studies of any note are available [19,20]. The aim of this paper is to present Raman and infrared spectra of natural hydrated double carbonates including pirssonite, gaylussite and tunisite. The paper is a part of systematic studies of vibrational spectra of minerals of secondary origin in the oxide supergene zone and their synthetic analogs.

2. Experimental

2.1. Minerals

Selected minerals were obtained from the Mineralogical Research Company and other sources including Museum Victoria. The samples were phase analysed by X-ray diffraction and for chemical composition by EDX measurements.

The origin of the minerals are as follows:

Pirssonite – Green River, Sweetwater Co., Wyoming labelled as pirssonite 1.
Pirssonite – Searles Lake, San Bernardino Co., California labelled as pirssonite 3.
The mineral pirssonite 3 is a type mineral [21] and is used as a standard or reference mineral (please go to p. 552 of Ref. [21]).
Gaylussite – Teels Marsh, Esmeralda County, Nevada. Gaylussite is listed on p. 241 of Ref. [21].
Tunisite – near Condorcet, Drome, France (p. 716 of Ref. [21]).

2.2. Raman microprobe spectroscopy

The crystals of halogenated carbonates were placed and oriented on the stage of an Olympus BHSM microscope, equipped with 10× and 50× objectives and part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a Charge Coupled Device (CCD). Raman spectra were excited by a HeNe laser (633 nm) at a resolution of 2 cm^{-1} in the range between 100 and 4000 cm^{-1}. Repeated acquisition using the highest magnification was accumulated to improve the signal to noise ratio. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer. In order to ensure that the correct spectra are obtained, the incident excitation radiation was scrambled. Previous studies by the authors provide more details of the experimental technique. Details of the technique have been published by the authors [22–25].

2.2.1. Mid-IR 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 64 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 adjustment, smoothing and normalisation were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'PEAKFIT' software package which 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 Lorentz–Gauss cross-product function with the minimum number of component bands used for the fitting process. The Gauss–Lorentz 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.

3. Results and discussion

The Raman spectra of two pirssonite minerals and gaylussite, shortite and quintinite in the 950–1450 cm^{-1} region are shown in Fig. 1. Adler and Kerr predicted from their infrared data that the carbonate units were crystallographically single units in the structure of pirssonite [8]. This was later confirmed by crytsallographic studies of synthetic pirssonite and gaylussite [26]. The Raman spectra of pirssonite as shown in Fig. 1a and b show a single intense band at around 1080 cm^{-1}. The position of this band is sample dependent. The band is observed at 1074 cm^{-1} for the second pirssonite mineral sample. A low intensity band at 1050 cm^{-1} is observed in the Raman spectrum and it is considered this band is a hot band. Adler and Kerr reported based on infrared spectra the position of the ν_1 band as 1068 cm^{-1} [8]. The carbonate unit in galylussite is on a C_1 site and is crystallographically distinct. Thus no splitting of the carbonate bands should be observed. This is confirmed by a single Raman band for galylussite at 1078 cm^{-1}. Adler and Kerr did not report an infrared band for gaylussite in the ν_1 position. In contrast the Raman spectrum of shortite (Fig. 1d) shows two Raman bands at 1070 and 1090 cm^{-1}. Adler and Kerr reported two infrared bands at 1069 and 1089 cm^{-1} in excellent agreement with the Raman data reported in this work [8].