



Spectroscopy Letters

An International Journal for Rapid Communication

ISSN: 0038-7010 (Print) 1532-2289 (Online) Journal homepage: <http://www.tandfonline.com/loi/lstl20>

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To cite this article: María M. Torres, Daniel Palacios, María C. D'antonio, Ana C. González-Baró & Enrique J. Baran (2016) Vibrational spectra of barium oxalate hemihydrate, Spectroscopy Letters, 49:3, 238-240, DOI: [10.1080/00387010.2015.1133651](https://doi.org/10.1080/00387010.2015.1133651)

To link to this article: <http://dx.doi.org/10.1080/00387010.2015.1133651>



Accepted author version posted online: 04 Jan 2016.



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Vibrational spectra of barium oxalate hemihydrate

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ABSTRACT

The infrared and Raman spectra of barium oxalate hemihydrate, $\text{BaC}_2\text{O}_4 \cdot 0.5\text{H}_2\text{O}$, were recorded and discussed on the basis of their structural peculiarities and in comparison with the spectra of the previously investigated calcium and strontium oxalates.

ARTICLE HISTORY

Received 10 November 2015
Accepted 15 December 2015

KEYWORDS

Barium oxalate; infrared spectra; Raman spectra

Introduction

Metallic crystalline oxalates are widely distributed in nature and have been observed in rocks, soil, water bodies, and among a great variety of living organisms, including plants and animals, in the form of the so-called biominerals.^[1] Magnesium and calcium oxalates are the only naturally found alkaline-earth minerals of this type.

Among this group, calcium oxalates constitute by far the most abundant and widely distributed metallic oxalates in nature.^[1] They are usually present either as $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ or as $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, whereas the corresponding trihydrate is relatively rare. The vibrational spectroscopic behavior of these oxalates, either natural or synthetic, has often been reported and discussed.^[1–4]

Some years ago, we investigated the two polymorphic forms of magnesium oxalate dihydrate, $\alpha\text{-MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, and $\beta\text{-MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, together with the respective anhydrous form.^[1,5]

Recently, the Fourier transform infrared spectra (FTIR) and FT-Raman spectra of the two known hydrates of strontium oxalate, namely $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and $\text{SrC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, have also been investigated.^[6]

Detailed vibrational spectroscopic information for barium oxalates is so far not available. Therefore, and to complement the available information on alkaline-earth oxalates, in this article, we present our results of an investigation of the corresponding hemihydrate, $\text{BaC}_2\text{O}_4 \cdot 0.5\text{H}_2\text{O}$.

Barium oxalate is known in the form of four hydrates, namely $\text{BaC}_2\text{O}_4 \cdot x\text{H}_2\text{O}$ with $x = 3.5, 2.0, 1.0,$ and 0.5 . The higher hydrates are relatively unstable, even at room temperature, degrading rapidly into the lower ones.^[7,8] The $\text{BaC}_2\text{O}_4 \cdot 0.5\text{H}_2\text{O}$ transforms to $\alpha\text{-BaC}_2\text{O}_4$ at 187°C .^[8]

Interest on barium oxalates also arises from the fact that it is one of the known precursors for the synthesis of different ceramic materials (cf. for example^[9–12]).

Experimental

Synthesis of $\text{BaC}_2\text{O}_4 \cdot 0.5 \text{H}_2\text{O}$

The compound was obtained by dropwise addition of 500 mL of a 0.2 M solution of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ to 500 mL of a 0.2 M solution of $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, under stirring and at room temperature. The white crystalline powder was filtered off, washed with water, and dried in air at room temperature.^[8,13]

The purity of the obtained product was confirmed by X-ray powder diffractometry, using a Philips PW 1710 diffractometer and Cu-K_α radiation ($\lambda = 1.5425 \text{ \AA}$), as well as by elemental chemical analysis (Carlo Erba EA 1108 elemental analyzer).

Spectroscopic studies

The infrared spectra in the spectral range between 4000 and 400 cm^{-1} were recorded as KBr pellets with a FTIR-Bruker-EQUINOX-55 spectrophotometer. Raman spectra, in the range $4000\text{--}100 \text{ cm}^{-1}$, were obtained with the FRA 106 Raman accessory of a Bruker IFS 66 FT-IR instrument, using the 1064-nm line of a solid state Nd:YAG laser for excitation.

Results and discussion

Structural characteristics of the compound

The structure of $\text{BaC}_2\text{O}_4 \cdot 0.5\text{H}_2\text{O}$ belongs to the triclinic space group $P(-1)$, with $Z = 4$.^[13] It contains two structurally independent Ba(II) ions coordinated to nine O-atoms at distances from 2.73(1) to 2.99(1) \AA and from 2.72(1) to 2.91(1) \AA , respectively. One of the oxalate ions is strictly planar, whereas the other one deviates significantly from planarity. The water molecules are only involved in weak hydrogen bonds in the structure.

Vibrational spectra

The measured FTIR and FT-Raman spectra of $\text{BaC}_2\text{O}_4 \cdot 0.5 \text{H}_2\text{O}$ are shown in Fig. 1, and the proposed assignments are presented in Table 1. These assignments, which are based on the previous studies mentioned above, are briefly discussed as follows:

Vibrations related to the O-H stretchings are appreciably split in the IR spectrum, a fact which has formerly also been observed on the spectrum of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (whewellite).^[2-4,14] The appearance of four bands clearly suggest that they are two structurally different water molecules in the unit cell ($Z=4$) of this crystal^[2,3] and, as the structural characteristics of H_2O in this compound have never been discussed in detail, this result is of peculiar interest. On the other hand, the position of these bands suggests the generation of relatively weak hydrogen bonds,^[15] in agreement with the basic available structural information.^[13]

Signals for the $\nu(\text{OH})$ vibrations could not be detected in the Raman spectrum. The corresponding deformational modes, $\delta(\text{H}_2\text{O})$, are surely overlapped by the very strong 1603 cm^{-1}

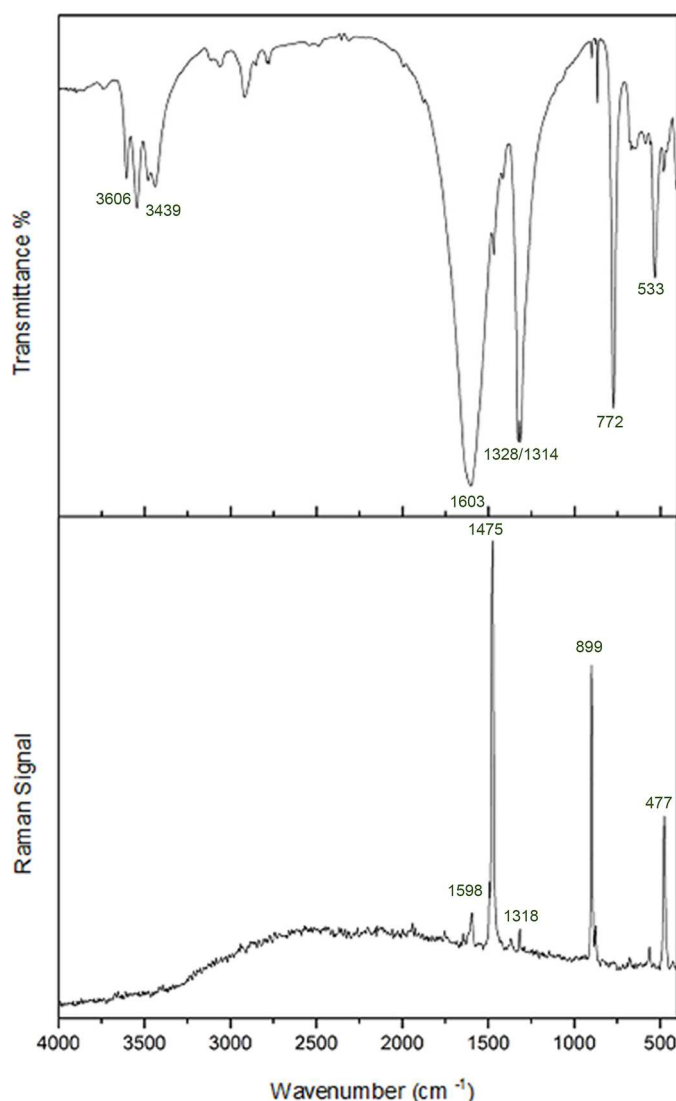


Figure 1. FT-infrared spectrum (above) and Raman spectrum (below) of barium oxalate hemihydrate in the spectral range between 4000 and 400 cm^{-1} .

Table 1. Assignment of the vibrational (infrared and Raman) spectra of barium oxalate hemihydrate (band positions in cm^{-1}).

Infrared	Raman	Assignment
3606 m, 3545 m		$\nu(\text{OH})$
3489 w, 3439 m		$\nu(\text{OH})$
3185 vw, 3064 vw		cf. text
2917 w, 2778 vw		cf. text
1603 vs	1598 w	$\nu_{\text{as}}(\text{CO}_2)$
1469 w, 1419 vw	1493 vw, 1475 vs	$\nu_s(\text{CO}_2) + \nu(\text{CC})$
1328 vs, 1314 vs	1371 vw, 1318 w	$\nu_s(\text{CO}_2)$
899 vw, 867 w	899 s, 876 w	$\nu(\text{CC})$
772 vs		$\nu(\text{CC}) + \delta(\text{CO}_2)$
668 sh, 648 m		$\rho(\text{H}_2\text{O})$
587 w	562 w	$\rho(\text{H}_2\text{O}) + \omega(\text{CO}_2)$
533 s		$\rho(\text{H}_2\text{O})$
482 w	477 s	$\omega(\text{CO}_2)$
407 m	424 vw	$\delta(\text{CO}_2)$
	351 w	$\rho(\text{CO}_2)$

vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder.

IR band. Notwithstanding, the first overtone of this vibration, probably shifted and intensified by Fermi resonance, could be located in the higher wavenumber region (the weak $3185/3064 \text{ cm}^{-1}$ doublet), as is also the case in the IR spectrum of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$.^[2,3]

The additional weak IR doublet at $2917/2778 \text{ cm}^{-1}$ probably originates in a combinational mode involving (CO_2) stretching modes. Similar combinations were also found in the case of whewellite^[14] and $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$.^[6]

The antisymmetric (CO_2) stretching vibration is the strongest IR band and appears only as a weak intensity Raman feature.

The strongest Raman line, located at 1474 cm^{-1} (with a weak satellite band at its higher energy side), has only weak IR counterparts.

The observed split of the $\nu_s(\text{CO}_2)$ vibrations may probably be related to the presence of the two mentioned structurally different oxalate anions.

In the spectral range below 1000 cm^{-1} , both the IR and Raman spectra resemble closely the respective $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ patterns.^[6,14,16]

The librational modes of the water molecules were also tentatively assigned in this region by comparison with the spectral data of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, and $\text{SrC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$.^[2,4,6,16]

No clear evidence was found for the presence of a $\nu(\text{Ba-O})$ vibration. In the calcium oxalates, such a mode was suggested to lie at around 500 cm^{-1} ^[16,17] and, therefore, it must be expected at lower energies in the present case, as was also suggested for the corresponding $\nu(\text{Sr-O})$ mode in the case of the strontium oxalates.^[6]

Conclusions

The results of this study are interesting because they allowed for the first time an insight into the vibrational-spectroscopic behavior of a barium oxalate, in this case the simplest of its hydrates, namely $\text{BaC}_2\text{O}_4 \cdot 0.5\text{H}_2\text{O}$, extending the general information available for alkaline-earth oxalates. The results show that the unit cell of the investigated hemihydrate ($Z=4$) contains two structurally different H_2O molecules, a conclusion which could not be derived from the previous

crystallographic study. Both the infrared and Raman spectra of this oxalate show close analogies to those of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (whewellite) and $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$. The results also extend the so far available information on the spectroscopic behavior of heavy metal oxalates (cf. also^[1,18,19]).

Acknowledgments

A.G.B. is a member of the Research Career from CONICET.

Funding

This work has been supported by the Universidad Nacional de la Patagonia Austral (UNPA), the Universidad Tecnológica Nacional (UTN), the Universidad Nacional de La Plata (UNLP), and the Consejo Nacional de Investigaciones Científicas y Técnicas de la República Argentina (CONICET).

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