

Infrared and Raman spectroscopic characterization of the carbonate mineral huanghoite – And in comparison with selected rare earth carbonates



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HIGHLIGHTS

- We have undertaken a study of huanghoite using vibrational spectroscopy.
- A comparison is made with spectra of other halogenated carbonates.
- Multiple carbonate stretching vibrations proved that there are non-equivalent carbonate units.
- Raman bands in the OH stretching region gives evidence for OH units in the huanghoite structure.

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ABSTRACT

Raman spectroscopy complimented with infrared spectroscopy has been used to study the rare earth based mineral huanghoite with possible formula given as $\text{BaCe}(\text{CO}_3)_2\text{F}$ and compared with the Raman spectra of a series of selected natural halogenated carbonates from different origins including bastnasite, parisite and northupite. The Raman spectrum of huanghoite displays three bands are at 1072, 1084 and 1091 cm^{-1} attributed to the CO_3^{2-} symmetric stretching vibration. The observation of three symmetric stretching vibrations is very unusual. The position of CO_3^{2-} symmetric stretching vibration varies with mineral composition. Infrared spectroscopy of huanghoite show bands at 1319, 1382, 1422 and 1470 cm^{-1} . No Raman bands of huanghoite were observed in these positions. Raman spectra of bastnasite, parisite and northupite show a single band at 1433, 1420 and 1554 cm^{-1} assigned to the $\nu_3(\text{CO}_3)^{2-}$ antisymmetric stretching mode. The observation of additional Raman bands for the ν_3 modes for some halogenated carbonates is significant in that it shows distortion of the carbonate anion in the mineral structure. Four Raman bands for huanghoite are observed at 687, 704, 718 and 730 cm^{-1} and assigned to the $(\text{CO}_3)^{2-}$ ν_2 bending modes. Raman bands are observed for huanghoite at around 627 cm^{-1} and are assigned to the $(\text{CO}_3)^{2-}$ ν_4 bending modes. Raman bands are observed for the carbonate ν_4 in phase bending modes at 722 cm^{-1} for bastnasite, 736 and 684 cm^{-1} for parisite, 714 cm^{-1} for northupite. Raman bands for huanghoite observed at 3259, 3484 and 3589 cm^{-1} are attributed to water stretching bands. Multiple bands are observed in the OH stretching region for bastnasite and parisite indicating the presence of water and OH units in their mineral structure. Vibrational spectroscopy enables new information on the structure of huanghoite to be assessed.

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1. Introduction

The carbonates are a group of over 150 naturally occurring minerals containing the essential structural building block $(\text{CO}_3)^{2-}$. Most of these minerals are relatively rare and quite often in association with other building blocks such as hydroxyls, halogens, sulfate, silicate, and phosphate. Among these minerals is the carbonate mineral huanghoite $\text{BaCe}(\text{CO}_3)_2\text{F}$. The mineral is one of

the synchysite mineral group which includes synchysite-Ce $\text{Ca}(\text{Ce},\text{La})(\text{CO}_3)_2\text{F}$, synchysite-Nd $\text{Ca}(\text{Nd},\text{Y},\text{Gd})(\text{CO}_3)_2\text{F}$, synchysite-Y $\text{Ca}(\text{Y},\text{Ce})(\text{CO}_3)_2\text{F}$. The importance of these rare earth minerals is that the minerals are a source of rare earths including lanthanum, yttrium and cerium.

There are a number of halogen containing carbonates including bastnaesite (often written as bastnasite and bastnäsite) $[(\text{Ce},\text{La})\text{CO}_3\text{F}]$, parisite $[(\text{Ce}_2,\text{Ca})(\text{CO}_3)_2\text{F}_2]$, northupite $[(\text{Na}_2,\text{Mg})(\text{CO}_3)_2\text{F}]$, and phosgenite $[\text{Pb}_2\text{CO}_3\text{Cl}]$ [1]. In fact this group of minerals supplies more than 70% of the world's supply of rare earths. In addition minerals based upon hydroxbastnasite are also

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known but little or no information is available for this mineral [2–4]. It is probable that the mineral decrespignyite-(Y) is structurally related to bastnäsite–synchysite–parisite group all of which adopt a hexagonal or at least a pseudo-hexagonal layered structure based upon repeat units of $\text{REE-CO}_3^{2-}(\text{F,OH})$ [5–7]. Bastnäsite is one of three carbonate-fluoride minerals. There is bastnäsite-(Ce) with a formula of $(\text{Ce,La})\text{CO}_3\text{F}$. There is bastnäsite-(La) with a formula of $(\text{La, Ce})\text{CO}_3\text{F}$. There is also bastnäsite-(Y) with a formula of $(\text{Y, Ce})\text{CO}_3\text{F}$. Most bastnäsite is bastnäsite-(Ce), and cerium is by far the most common of the rare earths in this class of minerals. Bastnäsite is closely related to the mineral parisite; both are rare earth fluorocarbonates. Parisite formula varies depending upon the locality of origin and may be generalized as $[\text{Ca}(\text{Ce,La,Nd})_2(-\text{CO}_3)_2\text{F}_2]$. Bastnasite forms a series with the mineral hydroxybastnasite. This latter mineral has a formula $[(\text{Ce,La})\text{CO}_3(\text{OH,F})]$ in which hydroxyl units substitute for the fluorine.

The crystal structures of most halogenated carbonates have been studied [8–10] including huanghoite [11–14]. However the crystal structure of decrespignyite is not known or defined. The crystal structure of parisite is said to be rhombohedral but the structure depends on the composition and origin of the mineral [8,15–19]. The infrared spectra of bastnasite, parisite and northupite have been published [20,21]. According to Farmer [1], bastnasite is hexagonal and the carbonate units lie on the 6(h) sites with point symmetry C_3 . The internal modes of the carbonate ion are symmetrical with little evidence of splitting. In the infrared spectra, the only evidence of symmetry reduction is the appearance of a low intensity band in the ν_1 position. The infrared spectra of parisite has been said to show low site symmetry and the presence of more than one carbonate type in the unit cell. Adler and Kerr observed splitting of ν_1 and ν_4 vibrational modes [20]. Farmer states that northupite has a highly symmetrical structure and is a rare example of a carbonate with a cubic structure [1]. The structure is complex with 16 formula units in the face-centred cubic cell. As a consequence of the reduction in symmetry from D_{3h} to C_3 , all bands are both infrared and Raman active.

Raman spectroscopy has proven most useful for the study of diagenetically related minerals as often occurs with carbonate minerals [22–24].

The objective of this paper is to report the vibrational spectroscopic study of a huanghoite mineral and relate the spectra to the molecular chemistry and the crystal chemistry of this carbonate mineral. We have characterized huanghoite using Raman and infrared spectroscopy, with support of scanning electron microscopy in the mineral characterization.

2. Experimental

2.1. Samples description and preparation

The huanghoite sample studied in this work was obtained from the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, Brazil, with sample code SAB-116. The sample is from the type locality for the mineral, the Bayan Obo deposit, Inner Mongolia Autonomous Region, China [25]. The mineral occurs in association with aegirine.

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

2.2. 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>).

Huanghoite single crystal up to 2 mm was coated with a 5 nm Au. Secondary Electron and Backscattering Electron images were obtained using a JEOL JSM-6360LV equipment. A qualitative and semi-quantitative chemical analysis in the EDS mode was performed with a ThermoNORAN spectrometer model Quest and was applied to support the mineral characterization.

2.3. Raman microprobe spectroscopy

Crystals of huanghoite were placed on a polished metal surface on the stage of an Olympus BSM microscope, which is equipped with 10 \times , 20 \times , and 50 \times 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 $\pm 1 \text{ cm}^{-1}$ in the range between 200 and 4000 cm^{-1} . Repeated acquisitions on the crystals using the highest magnification (50 \times) 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. The Raman spectrum of at least 10 crystals was collected to ensure the consistency of the spectra.

2.4. 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. The infrared spectra are given in the supplementary information.

Spectral manipulation such as baseline correction/adjustment and smoothing 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.

3. Results and discussion

3.1. Chemical composition of huanghoite

The SEM image of huanghoite sample studied in this work is shown in Fig. 1. The image shows a homogeneous fragment with no zonation or associated minerals. Qualitative chemical analysis shows a Ba, Ce and F carbonate with minor amounts of Nd (Fig. 2). The observed elements via SEM/EDS are in agreement with the chemical composition of huanghoite.

3.2. Spectroscopy of the carbonate anion

Nakamoto et al. [26] first published and tabulated the selection rules for unidentate and bidentate anions including the carbonate anion. The free ion, CO_3^{2-} with D_{3h} symmetry exhibits four normal vibrational modes; a symmetric stretching vibration (ν_1), an

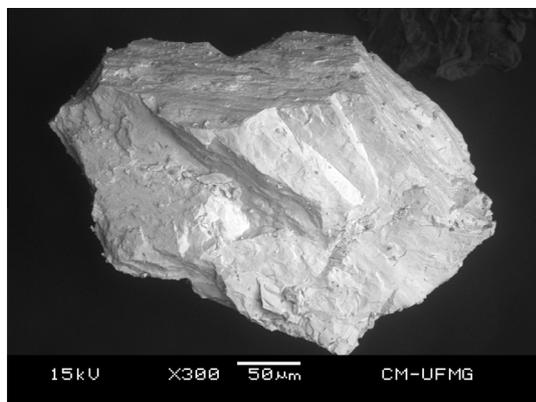


Fig. 1. Backscattered electron image (BSI) of a huanghoite crystal up to 0.5 mm in length.

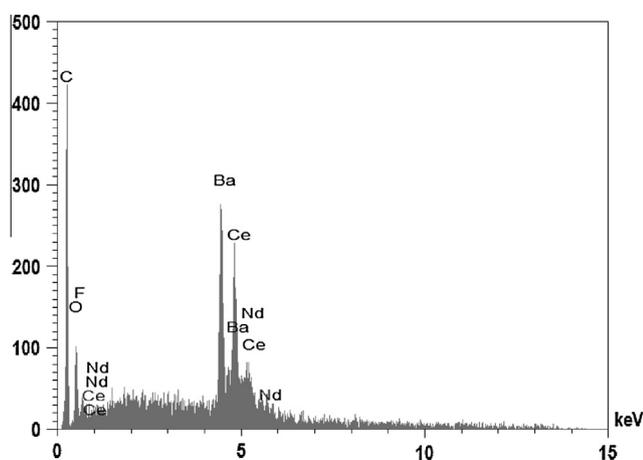


Fig. 2. EDS spectra of huanghoite.

out-of-plane bend (ν_2), a doubly degenerate asymmetric stretch (ν_3) and another doubly degenerate bending mode (ν_4). The symmetries of these modes are A_1' (R) + A_2'' (IR) + E' (R, IR) + E'' (R, IR) and occur at 1063, 879, 1415 and 680 cm^{-1} respectively. Generally, strong Raman modes appear around 1100 cm^{-1} due to the symmetric stretching vibration (ν_1), of the carbonate groups, while intense IR and weak Raman peaks near 1400 cm^{-1} are due to the antisymmetric stretch (ν_3). Infrared modes near 800 cm^{-1} are derived from the out-of-plane bend (ν_2). Infrared and Raman modes around 700 cm^{-1} region are due to the in-plane bending mode (ν_4). This mode is doubly degenerate for undistorted CO_3^{2-} groups. As the carbonate groups become distorted from regular planar symmetry, this mode splits into two components. Infrared and Raman spectroscopy provide sensitive test for structural distortion of CO_3^{2-} .

3.3. Spectroscopy

The Raman spectrum of huanghoite in the 100–4000 cm^{-1} spectral range is displayed in Fig. 3a. This figure shows the position and relative intensities of the Raman bands. There are large parts of the spectrum where no intensity is observed and thus, the spectrum is divided into sections depending upon the type of vibration being studied. The infrared spectrum of huanghoite over the 500–4000 cm^{-1} spectral range is shown in Fig. 3b. Again, there are large parts of the spectrum where no intensity is observed, and the spectrum may be subdivided into sections according to the type of vibration being examined.

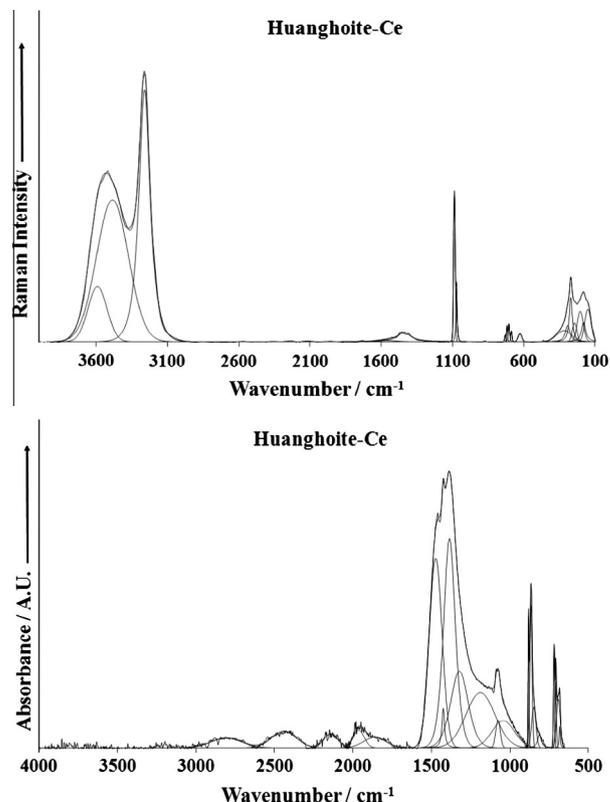


Fig. 3. (a) Raman spectrum of huanghoite over the 100–4000 cm^{-1} spectral range. (b) Infrared spectrum of huanghoite over the 500–4000 cm^{-1} spectral range.

The Raman spectrum of huanghoite in the 800–1400 cm^{-1} spectral range is displayed in Fig. 4a. The spectrum is dominated by a very intense sharp band at 1084 cm^{-1} assigned to the CO_3^{2-} ν_1 symmetric stretching mode. The main band has shoulders at 1072 and 1091 cm^{-1} . Low intensity Raman bands are found at 1350, 1371 and 1385 cm^{-1} . These bands are attributed to the CO_3^{2-} ν_3 antisymmetric stretching modes. In the infrared spectrum shown in Fig. 4b, the CO_3^{2-} ν_1 symmetric stretching mode is observed as a number of bands at 1057 and 1065 cm^{-1} with shoulder bands at 1048, 1072 and 1080 cm^{-1} .

The Raman spectra of huanghoite in the 500–800 cm^{-1} spectral range and in the 100–500 cm^{-1} spectral range are illustrated in Fig. 5. Four Raman bands for huanghoite are observed at 687, 704, 718 and 730 cm^{-1} and assigned to the $(\text{CO}_3)^{2-}$ ν_2 bending modes. Raman bands are observed for huanghoite at 619, 632 and 635 cm^{-1} and are assigned to the $(\text{CO}_3)^{2-}$ ν_4 bending modes. Raman bands are observed for the carbonate ν_4 in phase bending modes at 722 cm^{-1} for bastnasite, 736 and 684 cm^{-1} for parisite, 714 cm^{-1} for northupite. The Raman spectrum in the far low wavenumber region (Fig. 5b) shows a broad spectral feature which may be resolved into component bands at 150, 181, 244, 270, 292 cm^{-1} . These bands are simply described as lattice vibrations.

The Raman spectrum of huanghoite in the 2800–3800 cm^{-1} spectral range is reported in Fig. 6. Raman bands are observed at 3259, 3484 and 3589 cm^{-1} . These bands are attributed to water stretching vibrations. The observation of water bands in the Raman spectrum of huanghoite is unexpected as the formula suggests that no water is present.

A comparison may be made with the hydroxyl stretching region of the other halogenated minerals.

The Raman spectrum of bastnasite displays bands in similar positions at 3651, 3620, 3526, 3355, 3276, 3169 and 3203 cm^{-1} . The three higher wavenumber bands (3651, 3620, 3526 cm^{-1})

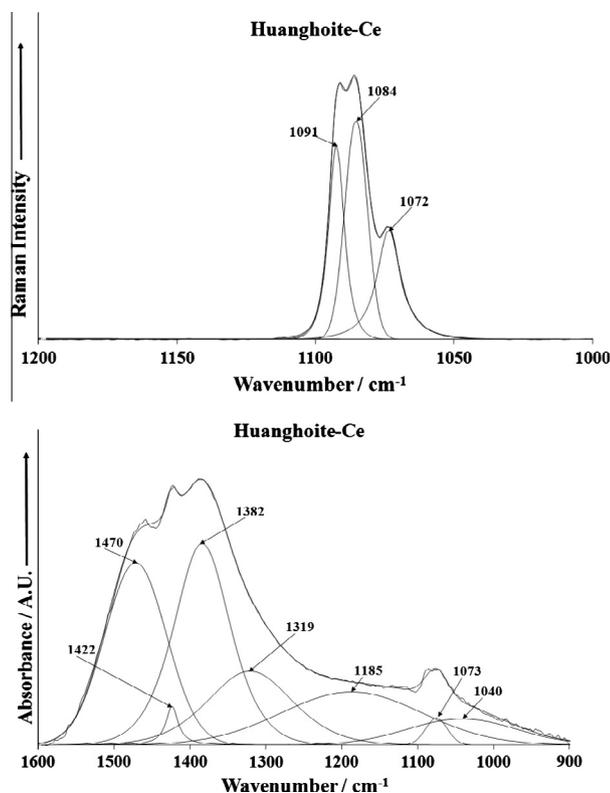


Fig. 4. (a) Raman spectrum of Huanghoite over the 800–1400 cm^{-1} spectral range. (b) Infrared spectrum of Huanghoite over the 500–1300 cm^{-1} spectral range.

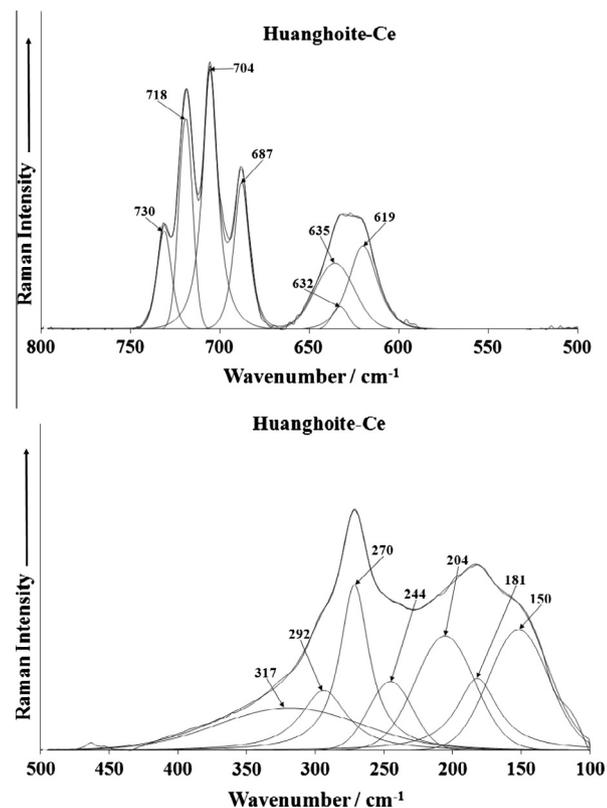


Fig. 5. (a) Raman spectrum of Huanghoite over the 300–800 cm^{-1} spectral range. (b) Raman spectrum of Huanghoite over the 100–300 cm^{-1} spectral range.

are most likely assignable to OH stretching vibrations. Raman spectra of a Chinese bastnasite have been published but no spectral

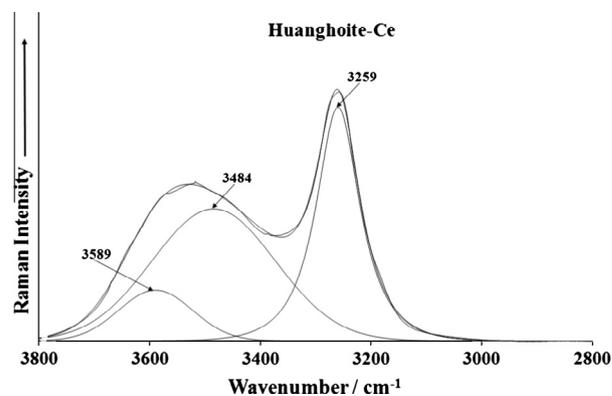


Fig. 6. (a) Raman spectrum of Huanghoite over the 2600–4000 cm^{-1} spectral range. (b) Infrared spectrum of Huanghoite over the 2600–4000 cm^{-1} spectral range.

information is available for comparison in this spectral region [27]. Another study reported some Raman data for rare earth carbonates [28,29]. However no spectral information in the OH stretching region was reported. The Raman spectrum of the hydroxybastnasite shows several bands at 3741, 3535, 3430, 3352 and 3317 cm^{-1} . For this mineral OH units replace F in a complex structure. It is possible that all of this set of bands is attributable to OH stretching vibrations. Aleksandrov described two types of bastnasites namely fluorobastnasite and hydroxybastnasite [29]. Another paper described the IR spectra in this spectral region with no detail except to state bands were observed [4]. For the mineral parisite broad bands in the OH stretching region are observed. Four Raman bands are observed at 3661, 3517, 3316 and 3180 cm^{-1} .

4. Conclusions

Raman spectroscopy has been used to characterize the mineral Huanghoite and a comparison made with other halogenated carbonates including bastnasite, hydroxybastnasite, parisite and northupite. The spectra of the minerals are dependent upon the mineral origin and its formulation. The halogenated carbonates are characterized by $(\text{CO}_3)^{2-}$ symmetric stretching modes in the 1078–1090 cm^{-1} spectral range. In the case of Huanghoite three Raman bands are found suggesting three non-equivalent $(\text{CO}_3)^{2-}$ units in the Huanghoite structure. This concept is supported by the observation of multiple bands in the antisymmetric stretching region. Infrared bands of Huanghoite occur at 1391, 1414, 1489 and 1547 cm^{-1} . These bands are assigned to the CO_3^{2-} ν_3 antisymmetric stretching mode. Two low intensity bands at 1504 and 1432 cm^{-1} for bastnasite are assigned to the ν_3 $(\text{CO}_3)^{2-}$ antisymmetric stretching mode.

The complexity of the symmetric stretching region is reflected in the $(\text{CO}_3)^{2-}$ bending region. Four Raman bands for Huanghoite are observed at 791, 815, 837 and 849 cm^{-1} and are assigned to the $(\text{CO}_3)^{2-}$ ν_2 bending modes. Two Raman bands at 865 and 845 cm^{-1} for bastnasite are assigned to the ν_2 $(\text{CO}_3)^{2-}$ bending mode. Raman bands are observed for decrespignyite at 694, 718 and 746 cm^{-1} and are assigned to the $(\text{CO}_3)^{2-}$ ν_4 bending modes.

Raman spectroscopy shows both the presence of water and OH units in certain selected minerals from this group even though the suggested formula does not show any OH units being present. The Raman spectra of bastnasite show bands at 3651, 3620, 3526, 3355, 3276, 3169 and 3203 cm^{-1} . For the mineral parisite broad bands in the OH stretching region with bands observed at 3516, 3310 and 3178 cm^{-1} . For parisite four Raman bands are observed at 3661, 3517, 3316 and 3180 cm^{-1} . A generalized formula may be written as $[\text{Ca}(\text{Ce},\text{La},\text{Nd})_2(\text{CO}_3)_2\text{F}_2]$. Raman spectroscopy suggests a general formula $[(\text{Ce},\text{La})\text{CO}_3(\text{OH},\text{F})\cdot x\text{H}_2\text{O}]$. The presence of OH-

anion suggest the partial substitution of F by OH and the existence of a F–OH series between huangoite-Ce and an undescribed mineral phase where OH is dominant in the structure.

Raman spectroscopy supports the concept that the position of the $(\text{CO}_3)^{2-}$ bands is a function of the chemical composition of the halogenated mineral. Farmer (pp 278) showed that the $(\text{CO}_3)^{2-}$ symmetric stretching band varied according to the ionic radius of the cation [1]. Raman spectroscopy supports the concept that the symmetry of the carbonate anion is maintained in the structure of bastnasite, parisite and northupite, even though many minerals have significant amounts of Ce, La or Y in the formula. The carbonate anion in the mineral hydroxybastnasite is of lower symmetry.

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