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SINGLE CRYSTAL RAMAN SPECTROSCOPY OF CERUSSITE

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ABSTRACT

Raman and infrared active modes of cerussite have been assigned according to their symmetry species, and compared to other aragonite group minerals. Small satellite bands at 823 and 1031 cm^{-1} to the low wavenumber side of the fundamental vibrations ν_2 and ν_1 , respectively, have been assigned to the isotopic substitutions of ^{13}C and ^{18}O . The Raman active ν_1 and ν_2 carbonate modes are observed at 1051 and 835 cm^{-1} . The absence of the B_{2g} component of the ν_1 and ν_2 vibrations has been explained by the small coupling between the A_g and B_{2g} modes. The Raman active ν_3 carbonate anti-symmetric stretching mode is observed at 1361(A_g), 1376 (B_{1g}), 1419 (B_{3g}) and 1477 (B_{2g}) cm^{-1} , while the corresponding infrared active bands are observed at 1396, 1432, and 1456 cm^{-1} . The Raman active ν_4 carbonate bending mode is observed at 673 (A_g), 668 (B_{2g}), 681 (B_{1g}), and 694 (B_{2g}) cm^{-1} . The corresponding infrared bands are observed at 670, 679, and 698 cm^{-1} . In both ν_3 and ν_4 , the factor group splitting between the B_{1g} and B_{3g} modes is 1 to 3 times smaller than the separation of the A_g and B_{2g} modes. Raman active lattice vibrations are detected at 120 (B_{3g}), 132 (A_g), 148 (B_{1g}), 152(B_{2g}), 174 (B_{2g}), 179 (B_{1g}), 213 (A_g), 226 (B_{3g}), and 243 cm^{-1} (B_{2g}). Corresponding infrared active bands are detected at 573, 543, 573, 423, 375, 290, 205, 165, 146, and 134 cm^{-1} . Raman bands at 949, 966, 989, 1000 and 1104 cm^{-1} and at 922, 946, 967, 988, 996, and 1007 cm^{-1} in the infrared spectra are assigned to combination and overtone bands. Raman bands at 1676 (A_g), 1689 (A_g), 1730 (B_{3g}), and 1740 (B_{1g}) cm^{-1} are ascribed to combination modes of $\nu_1 + \nu_4$ with bands at 2052 and 2092 cm^{-1} assigned to $2\nu_1$. Corresponding infrared bands are observed at 1729 and 1740 cm^{-1} ($\nu_1 + \nu_3$). Bands at 2359, 2409, 2471, and 2521 cm^{-1} are ascribed to $\nu_1 + \nu_3$, with broad bands at 1246 and 1323 cm^{-1} assigned to $2\nu_4$ modes.

INTRODUCTION

The carbonates are a group of over 60 naturally occurring minerals containing the essential structural building block $(\text{CO}_3)^{2-}$. Most of these minerals are relatively rare and often in association with other building blocks such as hydroxyls, halogens, sulphate, silicate, phosphate, etc. The common simple rock-forming carbonates can be divided in three main groups: 1) the calcite group, 2) the dolomite group and 3) the aragonite group. This paper will focus on cerussite as a member of the aragonite group, which contains the minerals aragonite (CaCO_3), cerussite (PbCO_3), strontianite (SrCO_3) and witherite (BaCO_3).

Aragonite is under atmospheric conditions metastable and therefore less commonly found in nature than calcite. Aragonite is often found in the calcareous skeletons of many organisms (e.g. shells of molluscs) (Compere and Bates, 1973; Markwitz et al., 1999; Ramaswamy and Srinivasan, 1977; Venec-Peyre and Jaeschke-Boyer, 1978). Carbonated waters may precipitate aragonite when the waters are warm, as around hot springs or geysers. It is sometimes observed as a constituent of evaporates associated with gypsum or celestine (in marls). Furthermore it has been found as a secondary mineral in cavities in volcanic rocks (Lindblom and Gerard, 1998), in the oxidized zones of ore deposits and in certain metamorphic rocks (e.g. blueschists in New Zealand and California). Witherite is a comparatively rare mineral. It is mostly found in low temperature hydrothermal veins associated with galena (PbS), anglesite (PbSO_4), barytocalcite ($\text{BaCa}[\text{CO}_3]_2$) and barite (BaSO_4). Strontianite is a low temperature hydrothermal mineral associated with witherite, barite, celestine, fluorite and lead-bearing minerals in limestones, marls or associated with gangue minerals in sulphide veins. Cerussite forms an important supergene lead ore formed by the action of carbonated water on galena (Klein, 2002). It is often associated with primary minerals such as galena and sphalerite ($[\text{Zn},\text{Fe}]\text{S}$) and secondary minerals such as anglesite, pyromorphite ($\text{Pb}_5[\text{PO}_4]_3\text{Cl}$), smithsonite (ZnCO_3) and limonite (hydrated impure variety of goethite, $\text{FeO}[\text{OH}]$).

The crystal structure of aragonite shows a nearly hexagonal closed packing of layers of Ca cations parallel to (001), but has been deformed by compression perpendicular to the layers. The carbonate groups are not located in the middle between two adjacent Ca cations and are rotated by approximately 30° either side in such a way that each oxygen atom has three neighbouring Ca atoms. The result of this arrangement of the carbonate groups is a lowering of the symmetry to orthorhombic compared to the trigonal calcite. In general the structure of the aragonite group minerals is governed by the radius of the metallic ion. Therefore the cell parameters of both strontianite and witherite are slightly larger than for aragonite (Table 1)(de Villiers, 1971; Jarosch and Heger, 1988; Jarosch, 1986; Martin and McCarthy, 1992). In the structure of aragonite small amounts of Ba or Sr can be incorporated. In contrast, both strontianite and witherite can incorporate a small amount of Ca, but a complete solid solution exists between strontianite and witherite. Cerussite has, like the other minerals in the aragonite group, the orthorhombic crystal structure with space group Pmcn. The morphology of cerussite crystals is often tabular on [010] as the crystal that is used in this study. Other forms include reticulated groups with the plates crossing each other at 60° angles (Deer et al., 1996).

A extensive array of literature exists for the spectroscopy of aragonite minerals (Bhagavantam and Venkatarayudu, 1939; Chevrier et al., 1992; Couture, 1947; Durman et al., 1985; Frech et al., 1980; Griffith, 1970; Jayasooriya and Kettle, 1984; White, 1974), but only a limited number of publications have focussed on cerussite. Chester and Elderfield (Chester and Elderfield, 1967) and Dorokhova et al. (Dorokhova et al., 1988) applied IR spectroscopy to identify a range of carbonates including cerussite. More fundamental work was done by Gervorkyan and Povarennykh (Gevorkyan and Povarennykh, 1969; Gevork'yan and Povarennykh, 1983) and Povarennykh (Povarennykh, 1972a; Povarennykh, 1972b) on the IR spectra of the aragonite group minerals. They observed correlations between the strength of the cation bond with the radicals and the position of the maximum in the absorption bands. The absorption bands shifted toward the long-wave region of the spectrum with increase in the bond strength. The bond strength regularly decreased in the aragonite group from 0.301 in aragonite to 0.119 in cerussite and the absorption band maximum in the IR spectra decreased simultaneously. Lin and Liu (Lin and Liu, 1997) used Raman spectroscopy to study phase behaviours of strontium and lead carbonates under quasi-hydrostatic conditions in a diamond-anvil cell up to 420 kbar at room temperature. The aragonite-type SrCO_3 (strontianite) and PbCO_3 (cerussite) were found to transform to their high-pressure polymorphs at approximately 350 and 170 kbar, respectively. Mode softening was observed for some of the Raman bands of both carbonates. For certain modes, furthermore, frequency shifts with the compression and decompression processes formed a hysteresis loop. The cause of the mode softening and hysteresis loop was interpreted to be caused by the spatial hindrance on the movement of the CO_3 groups in the crystal structure. Two relatively old papers focussed on the far-infrared spectra of selected metal carbonates including the aragonite group (Angino, 1967; Morandat and Lecomte, 1966).

To date no decisive explanation of the presence of satellite bands has been given. Furthermore, the assignment of low intensity bands, possibly due to overtone and combination bands, has been a matter of debate. In this paper the authors revisit the aragonite minerals to find the possible explanation of these low intensity bands in cerussite in relation to the other aragonite minerals.

EXPERIMENTAL

Origin of the samples

The cerussite sample was collected at Rum Jungle (Browns Prospect), Northern Territory, Australia. A single crystal of approximately 2 mm was used for oriented single crystal Raman microspectroscopy at room temperature. The cerussite sample was checked for phase impurities by X-ray diffraction techniques, Scanning Electron Microscopy and Energy Dispersive X-ray Analysis before Raman microscopic analysis of the selected crystal. The aragonite sample consists of an aggregate of needles from Liechtenstein (ref. 10 JTK). The strontianite sample consists of a large number of crystals from which a single crystal was removed for detailed analysis. The sample was collected at the type locality Strontian, Scotland (ref. 2909198507 JTK). A single crystal of witherite was collected at the Fallowfield Mine, Hexham, UK (ref. 2703198309 JTK). The room temperature Raman spectra were obtained on crystals still present in the host-rock for the witherite and strontianite. The spectra at 77 K were obtained on single crystals.

Synthetic cerussite was prepared from a 0.1M solution of $\text{Pb}(\text{NO}_3)_2$ to which 0.5M Na_2CO_3 was added at a rate of 10ml/min. The resulting cerussite was aged in contact with the solution for a period 24 hours at room temperature before filtering, washing and drying. The synthetic cerussite was then subject to XRD to check phase purity and SEM.

X-ray diffraction

The crystalline materials were characterised by X-ray powder diffraction (XRD). The XRD analyses were carried out on a Philips wide-angle PW 1050/25 vertical goniometer (Bragg Brentano geometry) applying $\text{CoK}\alpha$ radiation ($\lambda = 1.7902 \text{ \AA}$, 40 kV, 40 mA). The samples were measured at 50 % Relative Humidity in stepscan mode with steps of $0.02^\circ 2\theta$ and a scan speed of 1.00° per minute from 2 to $75^\circ 2\theta$.

Scanning electron microscopy

Scanning electron microscope (SEM) photos were obtained on a FEI QUANTA 200 Environmental Scanning Electron Microscope operating in this case at high vacuum and 15 kV. This system is equipped with an Energy Dispersive X-ray spectrometer with a thin window capable of analysing all elements of the periodic table down to carbon. For the analysis a counting time of 100 seconds was applied.

Raman microscopy

The micromount and single crystal samples were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10x, and 50x objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a Rayleigh filter system and a CCD detector. 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 resolution of approximately 4 cm^{-1} and a precision of $\pm 1 \text{ cm}^{-1}$ in the range between 120 and 4000 cm^{-1} . Repeated acquisitions 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. Crystals were orientated manually by visual inspection under the microscope. Differences in intensity may occur due to minor differences in the degree of visual focus of the microscope and variations in the optical quality of the crystal face. The Raman spectra of the oriented single crystals are reported in accordance with the Porto notation: the propagation directions of the incident and scattered light and their polarisations are described in terms of the crystallographic axes a, b and c. The notation may, for example read CABC. Here the first C is the direction of the incident light, A is the direction of the polarisation of the electric vector of the incident light, B is the orientation of the analyser and the second C is the direction of the propagation of the scattered light.

Spectra at low temperatures were obtained using a Linkam thermal stage (Scientific Instruments Ltd, Waterfield, Surrey, England). Samples were placed on a circular quartz disc, which fitted over the silver plate of the thermal stage. For spectra at 77 K, nitrogen gas from liquid nitrogen passed through a small hole in this plate immediately below the centre of the glass disc. Because of the increased optical path, spectra at 77K are noisier and require longer accumulation times. Spectra were

obtained by the co-addition of 10 60-second per point scans using a long working distance 50X (UWLD) objective. A lower Raman signal was obtained using this objective owing to the low numerical aperture of this long working distance objective. This, combined with the spherical aberration of the stage window, results in a decreased signal compared with that obtained without the thermal stage.

FT- Raman spectroscopy

The Fourier transform Raman spectroscopic (FT-Raman) analyses were performed on a Perkin Elmer System 2000 Fourier Transform spectrometer equipped with a Raman Accessory comprising a Spectron Laser Systems SL3001 Nd:YAG laser operating at a wavelength of 1064nm. The Linkam Thermal stage described above (operating at 77K) was connected to the FT-Raman spectrometer using a optic fibre coupling device. The natural cerussite spectra were collected by the co-addition of 256 scans with a spectral resolution of 0.1 cm^{-1} .

Infrared spectroscopy

Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer equipped with a Smart Endurance single bounce diamond ATR cell. Spectra over the range 4000 to 550 cm^{-1} 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^{-1} . Far infrared spectra were collected using the same spectrometer equipped with a polyethylene beam splitter in place of the KBr beam splitter. Samples (1mg) were ground and intimately mixed with CsI (200mg), followed by pressing it into a tablet at a pressure of 10 tonnes. Spectra were collected in transmission mode in a range from 120 to 600 cm^{-1} .

Spectral manipulations

Spectral manipulation such as baseline correction/adjustment and smoothing were performed using the GRAMS software package (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.

FACTOR GROUP ANALYSIS OF THE ARAGONITE GROUP

Aragonite is probably the most studied mineral of this group of carbonates. The classic paper is that of Couture (Couture, 1947), who measured the polarized Raman spectra of aragonite for the first time but many other papers have been published since. Bhagavantam and Venkatarayudu (Bhagavantam and Venkatarayudu, 1939) applied group theory to describe the infrared and Raman active modes of aragonite. The full factor group analysis was given by Frech et al. (Frech et al., 1980) and Griffith (Griffith, 1970) based on the orthorhombic structure of aragonite with D_{2h}^{16} ($Z = 4$). Here the site symmetry of the carbonate group is lowered to C_s . The bands observed are generally close to those of free carbonate although some splitting is observed due to the symmetry lowering in the minerals. Table 2 gives a summary of

the factor group analysis. The irreducible representations of the internal modes can be calculated from standard factor group analysis based on an orthorhombic crystal structure with space group Pmcn:

$$\Gamma_{\text{int}} = 4 A_g + 2 B_{1g} + 4 B_{2g} + 2 B_{3g} + 2 A_u + 4 B_{1u} + 2 B_{2u} + 4 B_{3u}$$

All of the *g*-modes are Raman active, while all of the *u*-modes are infrared active except for the *A_u* mode (Bhagavantam and Venkatarayudu, 1939; Frech et al., 1980). Jayasooriya and Kettle (Jayasooriya and Kettle, 1984) indicated that D_{3d}^3 can be used for a simpler factor group analysis for the lattice vibrations, as the aragonite group minerals can be considered to have a crystal structure which can be seen as a distortion of this space group. Durman et al. (Durman et al., 1985) suggested on the basis of single crystal Raman spectroscopy of cerussite had the C_{2v}^9 space group and that this mineral might therefore not be a member of the aragonite group. However, neutron diffraction data suggest that this is not the case, although cerussite does exhibit a somewhat distorted lattice in comparison with the other minerals of the aragonite group (Chevrier et al., 1992). Based on the analysis given in Table 2 one can expect eighteen Raman-active external modes, twelve of which are of the translational type and six of the rotational type. According to White (White, 1974) perturbations of the low symmetry aragonite structure results in three effects on the molecular modes of the carbonate anion. Firstly, relaxation of the selection rules that permits ν_1 to become active in the infrared and ν_2 active in the Raman. Secondly, the degeneracy is lifted and ν_3 and ν_4 each split in two components (site group splitting). Finally, because of interactions between the four carbonate molecules in the unit cell, each internal mode appears four times. These modes are distributed among different representations of the factor group and should therefore theoretically have different frequencies.

RESULTS AND DISCUSSION

The X-ray diffraction patterns indicate the samples are identical with the exception of two features. Firstly the synthetic cerussite has smaller crystal size shown by the increased broadness of the XRD peaks and the SEM images (Fig. 1a-b) and secondly the presence of a small amount of hydrocerussite in the synthetic sample's XRD pattern. In the natural cerussite sample a small amount of surface impurity, containing Fe and phosphate. The cerussite crystals were free of any impurities.

Fig. 2 gives an overview of the Raman spectra at room temperature and at 77 K of all minerals in the aragonite group. Clearly visible is the very strong ν_1 carbonate mode together with medium intensity split ν_3 and ν_4 modes, also seen is the weakly active ν_2 mode. The effect of cationic substitution may be clearly observed by inspection of the relative peak positions of the various modes of each mineral. The bands shift to higher wavenumbers with decreasing cationic radius and associated unit cell parameters (Table 1) from Ba^{+2} (witherite) to Sr^{+2} (strontionite) to Ca^{+2} (aragonite). The exception to this rule is cerussite where the effect of the polarisability of the cation is masked by the partial covalent nature of the lead carbonate bond (Alia *et al.*, 1997)

ν_1 carbonate region (900 – 1150 cm^{-1})

Fig. 3 shows the ν_1 mode of the carbonate ion in naturally occurring cerussite for four orientations, namely CC, CA, CB and AB. No attempt has been made to measure absolute intensities due to the varying optical quality of the crystal faces. However for each orientation a single band at 1054 cm^{-1} is the most obvious feature in this region. The presence of the ν_1 vibration as a singular band has also been noted in aragonite (Frech et al., 1980). An accompanying satellite band at 1031 cm^{-1} is clearly visible when the vertical scale is expanded (see inset, Fig 3). Other bands (not shown) are also observed at $949, 966, 989, 1000$ and 1104 cm^{-1} . Similar results are obtained for synthetic cerussite. On cooling, the ν_1 vibration for both the naturally occurring and synthetic cerussite shifts from 1054 cm^{-1} at 298 K to 1056 cm^{-1} at 77 K but no additional splitting could be detected. Factor group analysis predicts that the Raman active ν_1 vibration splits into an A_g and B_{2g} component, however the assignment of the B_{2g} mode is not obvious. The broad weak band at 1104 cm^{-1} corresponds with broad weak infrared bands (Fig. 4) at 1106 cm^{-1} may be attributable to the B_{2g} vibration. As this band is present at greater relative intensity in the cross-polarised spectra, the B_{2g} designation has merit. However factor group splitting is not significant enough to explain the large shift in energy from the A_g component. Another possible explanation is that this band is associated with a minor impurity of surface phosphate as seen in EDX, but since it is also present in the synthetic sample spectrum, this possibility can be discounted. Hydrocerussite also shows a weak band in this region of the Raman spectra, but owing to the absence of other hydrocerussite bands the 1104 cm^{-1} band cannot be attributed to the presence of hydrocerussite. The most likely cause is a combination band as will be discussed in a later section.

It is tempting to assign the satellite band at 1031 cm^{-1} to the B_{2g} mode. The presence of a low intensity band shifted by $20\text{-}30\text{ cm}^{-1}$ to lower wavenumbers of the ν_1 carbonate vibration in aragonites has been well documented, with many justifications given (Anderson, 1996; Cloots, 1991; Farmer, 1974). This band is also observed in synthetic cerussite where no impurities other than hydrocerussite are possible. As the naturally occurring cerussite does not have this impurity, hydrocerussite cannot be used to explain the results. Aragonite, witherite, and strontianite have ν_1 carbonate vibrations at $1054, 1060, 1072\text{ cm}^{-1}$, respectively, with satellite bands occurring at $1059, 1038, 1049\text{ cm}^{-1}$ in the Raman spectra. The FWHM of this band is much narrower than other combination bands. This and the fact that there is a nearly constant shift between the satellite band and the main ν_1 band in all aragonites suggest that combination bands are an unlikely explanation. It has been proposed that the most likely cause of this band is isotopic substitution in the carbonate (Cloots, 1991). Cloots (1991) showed that this band increased in intensity when aragonite was synthetically prepared with increased ^{18}O concentration. The satellite is always weak with an intensity of about 1% of the corresponding ν_1 band intensity. Frequency of stretching vibrations may be calculated from Equation [1] (Elderfield and Chester, 1971):

$$V = \frac{1}{2\pi c} \sqrt{\frac{k_o}{\mu}} \quad \text{Equation [1]}$$

where μ = reduced mass of participating atoms, k_o = force constant, V = vibrational frequency in wavenumbers and c = speed of light. Calculations using a reduced mass of $^{18}\text{O}\text{-}^{12}\text{C}$, predicts satellite bands at 1030 for cerussite, 1058 aragonite, 1034

witherite, and 1044 cm^{-1} strontianite, which are in good agreement with the experimental results.

The assignment of the satellite band to ^{18}O - ^{12}C allows the use of this band to quantify the oxygen isotopic ratio. This can have important implications for various areas in geology. Oxygen isotope fractionation between carbonates and (sea)water for example is well known to depend on temperature. In principle this allows one for example to determine the paleotemperatures of ancient oceans with a resolution better than 0.5 degrees C based on fractionation between calcite and seawater. The normal analysis method for stable isotopes involves very careful preparation of your samples under clean room conditions followed by measurement with ICP-MS (Inductively Coupled Plasma-Mass Spectrometry). It may be suggested that, when properly standardised, vibrational spectroscopy can be a rapid and much cheaper alternative to get an idea of the isotope fractionation in carbonates.

Combination bands are observed at 949 , 966 , 989 , and 1000 cm^{-1} in the Raman spectra and 922 , 946 , 967 , 988 , 996 , and 1007 cm^{-1} in the infrared spectra. These bands could stem from the combination of the ν_2 + lattice modes, as suggested by Donoghue et. al. (Donoghue et al., 1971), and or difference bands as suggested by Schutte and Buijs (Schutte and Buijs, 1961). Since Angino (Angino, 1967) observed that the far infrared spectra contained no absorption bands in the $90 - 30\text{ cm}^{-1}$ region, the possibility of combination and difference bands due to low wavenumber lattice bands can be discounted. The bands occurring to the low wavenumber side of the fundamental ν_1 vibration may be hot bands (vibrational transitions occurring from a excited state). The presence of these bands at greater intensity in cross-polarised spectra discredits this theory. Furthermore the presence of these bands in the 77K spectra unequivocally disproves the assertion that these are hot bands. Another explanation of the bands is multi-phonon processes involving low wavenumber fundamental internal vibrations and acoustic vibrations. Multi-phonon processes increase in intensity as the sample is cooled, as do the fundamental vibrations (Carter, 1998). Multi-phonon processes however increase in intensity relative to a fundamental at the same wavenumber, because the population of the ground state of the lower wavenumber bands is more affected by the temperature decrease than is the population of the higher energy bands (Carter, 1998). The 77K spectra do indeed show a relative increase in the low intensity band to the fundamental vibration, confirming the possibility of combination bands. Combination bands of the ν_4 + lattice bands and lattice band + lattice band may be expected to occur in the $800 - 1200\text{ cm}^{-1}$ region and is the most probable cause of the low intensity bands to high and low wavenumber sides of the fundamental ν_1 vibration. The suggested combinations are shown in Table 3.

The fact that all bands in this region may be satisfactorily assigned yet no definitive assignment can be made for the B_{2g} mode suggests that the B_{2g} mode is coincident with the A_g band. No further splitting of the ν_1 could be observed in a 77K FT-Raman spectrum of cerussite using a resolution of 0.1 cm^{-1} . This suggests that the factor group splitting, if present, is very small.

ν_2 carbonate region ($720 - 900\text{ cm}^{-1}$)

The Raman ν_2 carbonate vibration in cerussite is observed as a single band at 835 cm^{-1} (A_g) at 298K and 818 cm^{-1} at 77K, with the B_{1u} component appearing in the infrared

spectra at 839 cm^{-1} . Factor group analysis predicts this band to be split into an A_g and B_{3g} component in the Raman spectra. The B_{2g} component of the ν_2 like the B_{2g} component of the ν_1 is not clearly detected in the spectra, even at 77K or at high resolution. A low frequency satellite attributable to isotopic ^{13}C substitution in other carbonates (Cloots, 1991; Farmer, 1974; Sterzel, 1971; Sterzel and Chorinsky, 1968; Sterzel and Schnee, 1972; Sterzel et al., 1977) is also noted for cerussite at 823 cm^{-1} . The corresponding infrared band is observed at 824 cm^{-1} . Synthetic cerussite shows Raman bands at 837 cm^{-1} (A_g) and the satellite band at 823 cm^{-1} , with no observable B_{2g} component. Low intensity bands at 726, 734, 789 and 802 cm^{-1} are seen in the Raman Spectra of cerussite, which are also present in synthetic cerussite. As with the low intensity bands to high and low sides of the ν_1 vibration, the bands can not be explained by impurities. Subtraction bands of the 835 cm^{-1} band caused by absorption bands in the $90 - 30\text{ cm}^{-1}$ range of the can be ignored as cerussite has no low wavenumber absorptions (Angino, 1967). Likewise combination bands of that involve the 673, 668, 681, 694 cm^{-1} bands and $90-30\text{ cm}^{-1}$ bands can also be ignored. The suggested combination bands are shown in Table 3. Aragonite, witherite, and strontianite show ν_2 carbonate vibrations at 853, 847, and 853 cm^{-1} , with the cerussite appearing at lower wavenumbers caused by the partial co-valent bond between the lead and carbonate (Alia et al., 1997).

ν_3 carbonate region ($1350 - 1550\text{ cm}^{-1}$)

Four Raman bands at 1361(A_g), 1376 (B_{1g}), 1419 (B_{3g}) and 1477 cm^{-1} (B_{2g}) are attributed to the ν_3 carbonate bending mode in cerussite (Fig. 5) at 298K. These bands shift to 1364, 1378, 1427, and 1476 cm^{-1} , respectively, at 77K and no further splitting is apparent. The corresponding infrared active modes are seen at 1396, 1432, and 1456 cm^{-1} . The other aragonites show Raman ν_3 carbonate vibration at 1461, 1575 (aragonite), 1420, 1450, 1509, 1539 (witherite), and 1447, 1546 (strontianite) cm^{-1} . In aragonites, as the polarisability of the cation increases, the wavenumber of the vibration decreases. The Raman spectra of synthetic cerussite show no significant difference to that of the naturally occurring mineral.

ν_4 carbonate region ($600 - 720\text{ cm}^{-1}$)

Natural cerussite shows Raman bands (Fig. 6) at 673 (A_g), 668 (B_{3g}), 681 (B_{1g}), and 694 cm^{-1} (B_{2g}) can be attributed to the ν_4 bending modes of the carbonate ion at 298K. At 77K the Raman spectra revealed bands at 668, 672, 681, and 695 cm^{-1} . Infrared bands are observed at 670, 679, and 698 cm^{-1} in the infrared spectra. In both ν_3 and ν_4 , the factor group splitting between the B_{1g} and B_{3g} modes is 1 to 3 times smaller than the separation of the A_g and B_{2g} modes. In light of this fact it is surprising that the expected ν_1 band splitting for cerussite into an A_g and B_{2g} component is not observed. Synthetic cerussite shows Raman bands in the exact band positions as seen in naturally occurring cerussite. Aragonite shows ν_4 bands at 701, 705, and 716 cm^{-1} . Witherite shows bands at 689, 699, and 710 cm^{-1} , with strontianite showing bands at 696, 701, and 710 cm^{-1} showing the same trend with the cation polarisability as observed in the other modes.

Lattice Vibrations ($120 - 600\text{ cm}^{-1}$)

Lattice vibration bands of cerussite (Fig.7) are detected at 120 (B_{3g}), 132 (A_g), 148 (B_{1g}), 152(B_{2g}), 174 (B_{2g}), 179 (B_{1g}), 213 (A_g), 226 (B_{3g}), and 243 cm^{-1} (B_{2g}). It is predicted from factor group analysis $5A_g + 5B_{2g} + 4B_{1g} + 4B_{3g}$ modes to be present. However, due to the increased mass of the cation with respect to the other aragonites,

there is a general shift of the lattice vibrations to lower frequencies and so some bands can be expected to be below the cut off frequency of the Raman spectrometer, in this case 120 cm^{-1} . Corresponding Mid and Far infrared active bands for cerussite are detected at 573, 543, 573, 423, 375, 290, 205, 165, 146, and 134 cm^{-1} .

Overtone and combination bands

Raman bands are observed at $1676\text{ (A}_g\text{)}$, $1689\text{ (A}_g\text{)}$, $1730\text{ (B}_{3g}\text{)}$, and $1740\text{ (B}_{1g}\text{)}\text{ cm}^{-1}$. The possibility exists for overtones in this region from ν_2 . It would be expected however that the energy of this vibration would be less than direct $2\nu_2$ product due to anharmonicity. Assignment of these bands to $\nu_1 + \nu_4$ with bands at 2052, and 2092 cm^{-1} assignable to $2\nu_1$ is more probable. Infrared bands are observed at 1729, 1740 cm^{-1} ($\nu_1 + \nu_3$). Bands are observed at 2359, 2409, 2471, and 2521 cm^{-1} due to $\nu_1 + \nu_3$, with band attributable to $2\nu_4$ detected as broad bands at 1246 and 1323 cm^{-1} .

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Table captions

- Table 1** Crystallographic data of the aragonite group minerals
Table 2 Factor group analysis of the carbonate ion in the aragonite group mineral structures (orthorhombic, Pmcn, D_{2h}^{16})
Table 3 Suggested combination band assignment
Table 4 Factor group analysis of CO_3^{2-} internal vibrations

Figure captions

- Figure 1a** SEM image of cerussite
Figure 1b SEM Image of synthetic cerussite
Figure 2 The Raman spectra of a) cerussite 298K, b) 77K, c) witherite 298K, d) 77K, e) strontianite 298K, f) 77K, g) witherite 298k, and h) 77K
Figure 3 Raman spectra in the ν_1 region for orientated cerussite crystals
Figure 4 The Infrared spectrum of cerussite
Figure 5 Raman spectra in the ν_3 region for orientated cerussite crystals
Figure 6 Raman spectra in the ν_4 region for orientated cerussite crystals
Figure 7 Raman spectra in the lattice region for orientated cerussite crystals

Table 1 Crystallographic data of the aragonite group minerals. (de Villiers, 1971; Jarosch and Heger, 1988; Jarosch, 1986; Martin and McCarthy, 1992)

Mineral	Chem. formula	Orthorhombic	Space group	a (Å)	b (Å)	c (Å)
Aragonite	CaCO ₃	2/m 2/m 2/m	<i>Pmcn</i>	4.96	7.97	5.74
Strontianite	SrCO ₃	2/m 2/m 2/m	<i>Pmcn</i>	5.11	8.41	6.03
Cerussite	PbCO ₃	2/m 2/m 2/m	<i>Pmcn</i>	5.18	8.52	6.15
Witherite	BaCO ₃	2/m 2/m 2/m	<i>Pmcn</i>	5.31	8.90	6.43

Table 2 Factor group analysis of the carbonate ion in the aragonite group mineral structures (orthorhombic, Pmcn, D_{2h}^{16})

Free symmetry D_{3h}	Site symmetry C_s	Factor group D_{2h}	Activity
ν_1 A_1'	$4A'$	$4A_g$	Raman
ν_2 A_2''		$4B_{2g}$ $4B_{1u}$ $4B_{3u}$	Raman Infrared Infrared
ν_3 E'	$2A''$	$2B_{1g}$	Raman
ν_4 E'		$2B_{3g}$ $2A_u$ $2B_{2u}$	Raman Inactive Infrared

Lattice vibrations

$$\Gamma = 5A_g + 4B_{1g} + 5B_{2g} + 4B_{3g} + 4A_u + 4B_{1u} + 3B_{2u} + 4B_{3u}$$

Table 3 Suggested combination band assignment

Band position /cm⁻¹	Explanation	Expected frequency /cm⁻¹
1104	2 x 573	1146
1007	2 x 543	1086
989	573 + 423	996
988	573 + 423	996
967	543 + 423	966
949 / 946	375 + 573	948
922	542 + 375	917
802	375+423	798
789	573+209	782
733	573+165	738
725	573+146	719
698/695	573+120	693
681/679	543+132	675
672	543+132	675
668	543+120	663

Table 4 Factor group analysis of CO₃²⁻ stretching vibrations

Mode of Carbonate	D _{2h}	Cerussite (298K)	Witherite (298K)	Strontianite (298K)	Aragonite (298K)
v ₁	A _g	1054	1060	1072	1054
	B _{2g}				
	B _{1u}	1051			
	B _{3u}	1053			
v ₂	A _g	837	847	853	853
	B _{2g}				
	B _{1u}	839			
	B _{3u}				
v ₃	A _g	1361	1420	1447	1461
	B _{2g}	1477	1450		
	B _{1u}	1432			
	B _{3u}	1456			
	B _{1g}	1376	1509	1546	1575
	B _{3g}	1419	1539		
	A _u	inactive			
	B _{2u}	1396			
v ₄	A _g	673	689	696	701
	B _{2g}	694	699	701	705
	B _{1u}	679			
	B _{3u}	670			
	B _{1g}	681	710	710	716
	B _{3g}	668			
	A _u	inactive			
	B _{2u}	698			