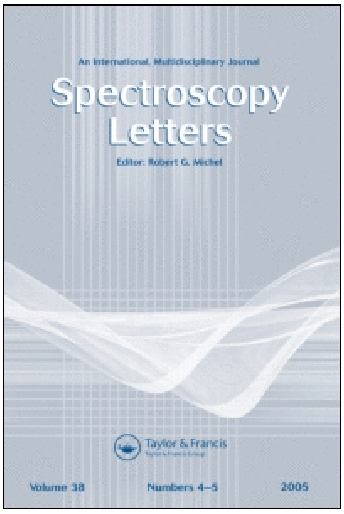


Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

THE INFRA-RED AND RAMAN SPECTRA OF ULTRA-FINE CALCITE

Linhai Yue[a]; Miao Shui[a]; Zhude Xu[a]
[a] Department of Chemistry, Zhejiang University, Hangzhou, China

To cite this Article Yue, Linhai , Shui, Miao and Xu, Zhude(2001) 'THE INFRA-RED AND RAMAN SPECTRA OF ULTRA-FINE CALCITE', Spectroscopy Letters, 34: 6, 793 — 802

To link to this Article: DOI: 10.1081/SL-100107901

URL: http://dx.doi.org/10.1081/SL-100107901

SPECTROSCOPY LETTERS, 34(6), 793–802 (2001)

THE INFRA-RED AND RAMAN SPECTRA OF ULTRA-FINE CALCITE

Linhai Yue, Miao Shui, and Zhude Xu*

Department of Chemistry, Zhejiang University,
Hangzhou 310027, China

ABSTRACT

In this study, three ultra-fine calcite samples having similar particle size but presenting different agglomeration state were synthesized. SEM and TEM measurements, Infrared and Raman analysis were used to view how the structure may possibly affect their spectrum characteristics.

Key Words: Ultra-fine calcite; Lattice vibration; Agglomeration state; Far-infrared and Raman spectra

INTRODUCTION

Calcium carbonate is one of the most widely used fillers in many industrial applications such as plastics, rubber, papermaking and medicine. Recently it is found that the nano scale calcium carbonate has much more advantages than the commonly used sorts with normal size. Its

---

*Corresponding author.

novel characteristic has attracted wide research interests. Spectroscopic property is a critical means in the characterization. However, as to the recently available literature, most of the IR and Raman investigations about calcium carbonate have focused on the spectra behavior of different phases but very few dealt with size effect. For example, the mid and far infrared spectra of calcite, vaterite, aragonite and amorphous calcium carbonate in room temperature and under liquid nitrogen atmosphere were systematically studied by Anderson[1]. Nicol[2,3] and Adams[4] also reported the mid-infrared and Raman characteristic of the calcium carbonate and carbonate synthesized under higher temperature and pressure. As to the influence of the particle size on the spectrum behavior, Ye[5] has suggested that the red shift of stretching vibration assimilation band and the blue shift of the out-of-plane bending vibration assimilation band coexists in the mid-infrared area of the nanocrystalline MgO. But, the study on the change of IR and Raman spectra stemming from the particle size change, especially on the crystal agglomeration states, is seldom reported.

EXPERIMENTAL

Purified CO_2 gas ($20 \sim 40\%$ concentration, diluted with N_2) was bubbled through $5 \sim 10\%$ $Ca(OH)_2$ solution until the pH value reached at $7 \sim 8$. The precipitate was filtered, dried at 110℃ to steady weight and then sifted through 320 mesh. Under altered reaction conditions three nano-particle $CaCO_3$ samples with different particle size and agglomeration state were obtained, referred to as 980227c, 980602 and 980622 respectively[6]. Analytical grade calcite (99.99%, $5 \sim 20\,\mu m$ particle size estimated by SEM) was used as the standard reference without the structural broadening.

The IR spectra were recorded at room temperature in the region of $400 \sim 3600\,cm^{-1}$ on a Nicolet model 5DX FT-IR spectrometer using KBr pellets. The far infrared spectrum was measured on a Bio Rad FTS-185 spectrometer. The calcite powder was mixed up evenly with the paraffin and fixed in-between the polyethylene films while measuring. The spectroscopic resolution is $4\,cm^{-1}$.

The Raman spectrum was recorded on a Bruker RFS100 FT-Raman spectrometer. The resolution is $4\,cm^{-1}$. The RFS 100 was equipped with a low-noise, diode-pumped Nd:YAG laser, which generates $1064\,cm^{-1}$ laser beam as stimulating source with an output power of 500 mW.

RESULTS AND ANALYSIS

The Microstructure of the Ultra-fine Calcite

The following three images in Fig. 1 are SEM or TEM images of sample 980227c, 980602 and 980622 respectively. Figure 1a, the TEM image, shows that sample 980227c has a cubic structure crystal lattice with the particle size ranged from 40 to 80 nm. The crystal lattices of both samples 980622 and 980602 seem an integrated form. As shown in Fig. 1c, sample

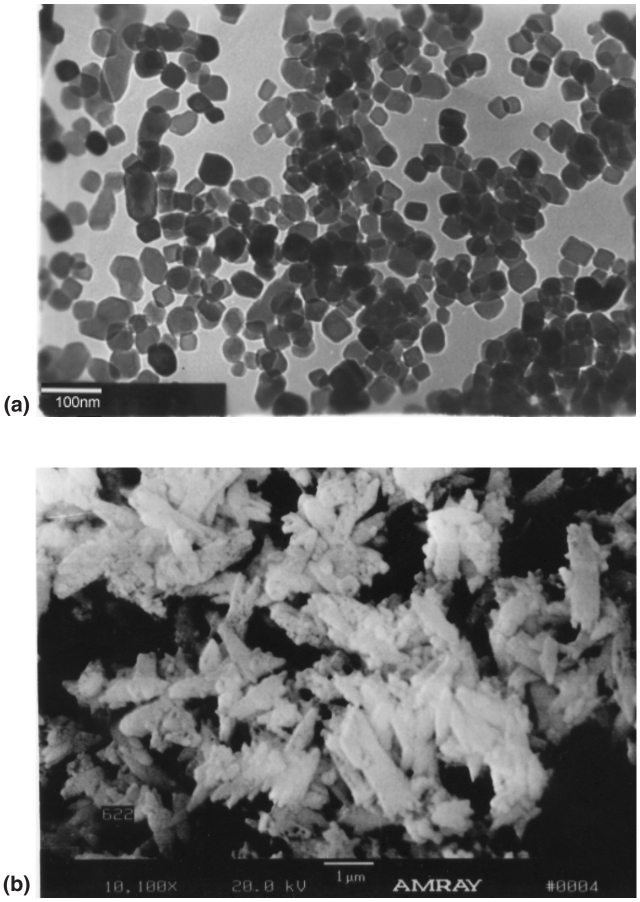
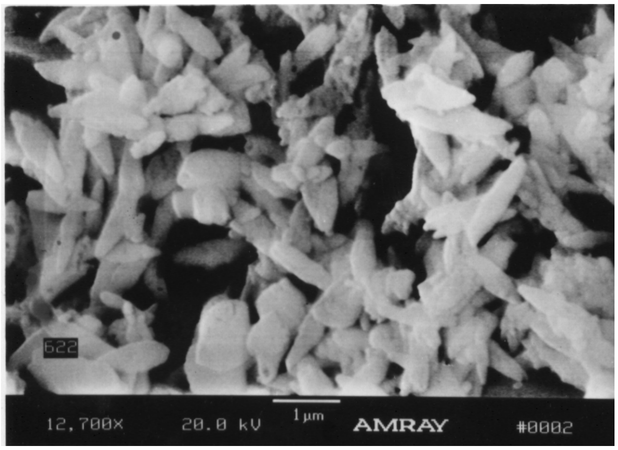


Figure 1. (a) TEM image of sample 980227c, (b) SEM image of sample 980602, (c) SEM image of sample 980622.

(*continued*)



(C)

Figure 1. Continued.

980622 has a shuttle-form structure with the size of about 1.5 ~ 2 nm long and 300 ~ 600 nm wide. Besides, there are also a few 100 ~ 400 nm cubic grains mixed within those shuttle-form grains. Figure 1b shows that most of the crystal grains in sample 980602 have loose shuttle-form structure, about 1 ~ 1.5 µm long and 200 ~ 600 nm wide, with a considerable number of 100 ~ 500 nm cubic grains. It seems that the shuttle-form structure is conglomerated from the base cubic structure and sample 980602 represents a state being in this conglomeration process.

The Infrared Behavior of Nano-crystalline $CaCO_3$

The free carbonate ion belongs to the point group D_{3h} and therefore should have four normal vibration modes, namely A_1'(? $_1$), A_2''(? $_2$) and two double degenerated E'(? $_{3a,3b}$ and ? $_{4a,4b}$). ? $_1$ is the symmetrical stretching vibration of C=O double bond with Raman activity. ν_2 is the out-of-plane bending vibration and is IR active. ν_3 is the non-symmetrical stretching mode of C=O double bond while ν_4 is the in-plane bending vibration mode of OCO. They are both Raman and IR active. Figure 2 shows the mid-infrared spectra of the three ultra-fine samples together with the reference. The above mentioned three IR active modes have all appeared in these spectra. The absorption bands peaked at 1425 cm^{-1}, 874 cm^{-1}, and 712 cm^{-1} in the spectrum of the reference $CaCO_3$ are assigned as ν_3, ν_2 and ν_4 respectively. It seems the ν_3 band is strong and broad while ν_2 and ν_4 bands are weak and

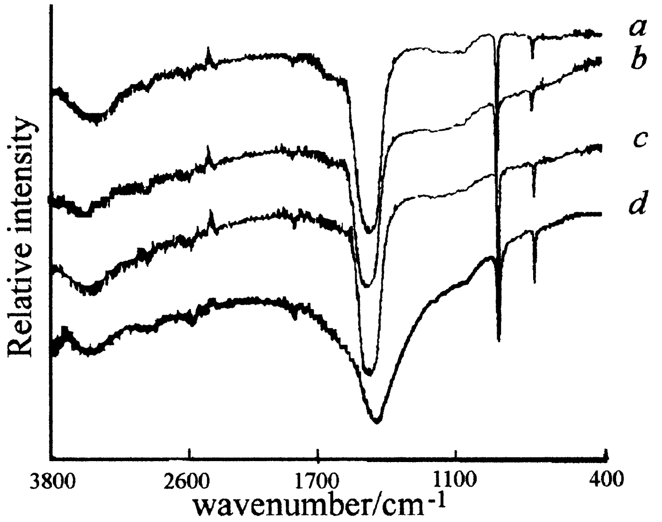


Figure 2. The infrared spectrum for (a) 980227c, (b) 980602, (c) 980622, (d) reference calcite.

narrow. Differing from the reference sample, the ν_3 absorption bands of all three ultra-fine samples are abnormally narrow and each has an obvious $40\,\mathrm{cm}^{-1}$ blue shift. According to the absorption band positions and comparing with the standard infrared spectrum of calcite[7], also Judging from the criteria of non-split ν_2 and ν_4 suggested by Andersen[1], the crystal structure of both the reference sample and the other three ultra-fine samples are all assigned as calcite. In general, size effect on the spectral property would be manifest with the diminution of particle size especially when it reduces to nano scale. This size effect usually causes a blue shift of IR absorption band. XRD results show that the crystal lattice has a contraction tendency with the diminution of particle size[8]. This may shorten the mean bond length hence lift the stretching vibration frequency. In addition, the interface of nano-scale material weighs much more in volume fraction. The defects and the insufficient coordination number occurring in the interface layer make the chemical or physical adsorption on surface easy to implement. In the case of hydrogen atom absorption, for example, the formation of hydrogen bonds by the absorbed hydrogen atom will usually cause a blue shift to IR absorption. The relatively large blue shift of ν_3 in the IR spectra of the ultra-fine calcite may be a comprehensive representation of all above mentioned effects.

Andersen[1] has suggested that the strong and broad ν_3 absorption band originate from several overlapping bands which are resulted from the combination of the lattice vibrations A_{2u} (354 cm^{-1}) and $2E_u$ (311 cm^{-1}, 227 cm^{-1}) with the molecular normal modes ν_2 and ν_4. Rao[9] suggested that although the inter-molecular force in the calcium carbonate crystalline is relatively weak so that it could not greatly influence the molecular vibration mode. But it often can split the degenerated vibration energy level and change the relative intensities of the molecular or lattice vibration modes. The split double peaks of ν_3 and ν_4 in the IR spectra of aragonite and vaterite are the case.

Figure 3 shows the far IR spectra of the reference and the three ultra-fine samples in the range of 400 cm^{-1} to 100 cm^{-1}. The absorption intensities of the lattice modes for the three ultra-fine samples are much weaker than that of the reference calcite. This may give an explanation to the narrowing ν_3 band in the case of ultra-fine samples. Furthermore, there exists difference of peak positions. Sample 980227C, consisting mainly of cubic grains, has similar peak positions as the reference calcite while new lattice vibration peaks have appeared in the case of sample 980602 and 980622. As described above, their crystal gains are agglomerated from small cubic grains. The peak position change may result from the direction character of bridge

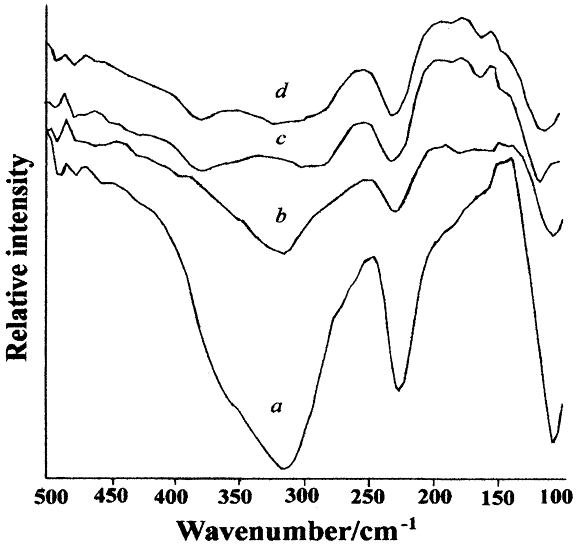


Figure 3. The far infrared spectrum for (a) reference calcite, (b) 980227c, (c) 980602, (d) 980622.

bonds between the grain interface. However, it may due to much more complicated reasons because of the inconsistency about the far IR peak positions of calcite in reported literatures. The lattice vibration frequencies obtained by our experiments together with those reported in literatures are listed in Table 1.

The Raman Spectra of Nano-crystalline $CaCO_3$

Figure 4 shows the Raman spectra of the reference calcite and the three ultra-fine samples in the range of $3500\,cm^{-1}$–$50\,cm^{-1}$. The peak position of the reference calcite and the three ultra-fine samples are basically the same. Analyzing according to molecular point group, the five peaks in the spectra are assigned to one A_{1g} mode and 4 pairs of E_g double degenerated vibrations. A_{1g} is a molecular vibration and consists of two carbonate ions vibrating at the same phase. Each ion has the A_I' symmetry of the free carbonate ion. The corresponding peak appears at $1088\,cm^{-1}$ in the spectrum. Two pairs of double degenerated vibration with E_g symmetry are also internal modes consisting of two carbonate ions with the E' symmetry of the free carbonate ion. The corresponding vibration frequencies are $714\,cm^{-1}$ and $1432\,cm^{-1}$ respectively. The other two pairs of E_g symmetry vibrations are lattice vibration modes. One is involving the libration motion and the other refers to the translation motion of the two carbonate ions. The corresponding peaks are located at $156\,cm^{-1}$ and $283\,cm^{-1}$. The Raman scattering peaks of the three ultra-fine samples including both molecular and lattice vibration modes are much weaker than those of reference calcite. The sequence of intensity (from strong to weak, note the different vertical scale in Fig. 4 is 980227c, 980602, and 980622, having similar trend as in the far-IR case. We suggest that the diminution of the grain size may result in the

Table 1. Observed Lattice Frequencies and Those Reported in Literatures for Calcite (in cm^{-1})

Reference	980227c	980602	980622	A[1]	B[1,10]	C[11]	D[10]	E[4]
312	315	378	380	312	360	342	338	303
228	230	301	324	229	335	309	310	297
106	108	289	304	106	182	229	176	223
		230	229		106	109	106	102
		185	185				86	92
		162	162					
		115	112					

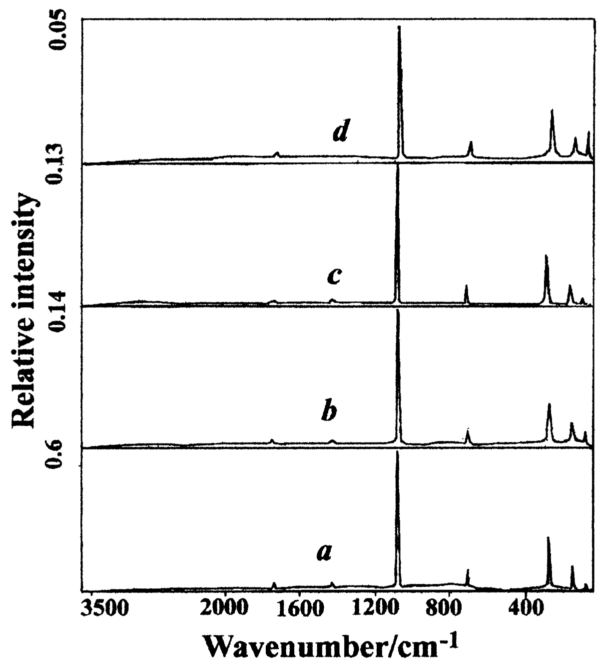


Figure 4. The Raman spectra for (a) reference calcite, (b) 980227c, (c) 980602, (d) 980622.

augmentation of the crystal lattice defects and weakening of the crystal field as well. It further reduces the lattice vibration intensity of ultra-fine calcite. This may explain the intensity difference between the three ultra-fine samples and the reference calcite. As for the differences among the three ultra-fine samples having similar grain size, the agglomeration states may play an important role in the scattering intensity.

The Raman scattering intensity can be presented as

$$I = k_{\omega}\omega_0^4(\alpha)_0^2E_0^2 \tag{1}$$

In which, I is the Raman scattering intensity. α is the degree of molecular polarization. ω_0 and E_0 are the angular frequency and electric field intensity of the incoming radiation respectively. Under the same experimental conditions, ω_0 and E_0 are basically unvaried. So that the weakening of internal vibration modes may be result from the variation of molecular polarization. Compared with the reference calcite, the large lattice strain lessens the degree of polarization and further weakens the internal vibration. The force field at the interface of the agglomeration grains also influences the degree of polarization hence the Raman scattering intensity.

CONCLUSION

By analysis of IR and Raman spectra for three ultra-fine calcite having similar crystalline grain but different agglomeration state, it is found the ultra-fine calcite has much different spectrum characteristics from the normal sized calcite. Compared with the reference calcite, the absorption band of asymmetric stretching mode ν_3 for the three ultra-fine samples is abnormally narrow and has an obvious blue shift about $40\,\mathrm{cm}^{-1}$ in mid-IR region. In the far-IR region, the lattice vibrations of ultra-fine samples were distinctly weakened. There is also evidence that the agglomeration states would affect the lattice vibration modes. Comparing our experimental results with the literature reports, it is suggested that increased defects and strain of crystal lattice in nano-particle calcite would weaken the crystal field effect hence weaken the lattice vibrations in the far infrared region. As a consequent result, the overlapping peaks around ν_3 band, which are the combination of molecular normal modes with lattice modes, attenuate greatly. It makes the ν_3 band much narrow. This size effect of crystalline grain also appears very clearly in the Raman spectra. Although the peak positions remain basically unchanged but the Raman intensity is decreased a lot for the ultra-fine samples. In addition, the spectral intensity decreases with the augmentation of agglomeration degree. A possible explanation is that the force field at the interface of agglomeration grains may change the degree of polarization and further change Raman scattering intensity.

REFERENCES

1. Andersen, F.A.; Brecevic, Ljerka. Acta Chemica Science **1991**, *45*, 1018.
2. Fong, Mei Y.; Nicol, M. J. Chem. Phys. **1971**, *54*, 579.
3. Nicol, M.; Ellenson, William D. J. Chem. Phys. **1972**, *56*, 677.
4. Adams, David M.; Williams, Alan D. J. Chem. Soc. Dalton Trans. **1980**, *8*, 1482.
5. Ye, Xisheng; Sha, Jian; Jiao, Zhengkuan; Zhang, Lide. Function Material **1998**, *29*, 287.
6. Cai, Juxiang; Yue, Linhai. Inorganic Industry **1995**, *5*, 7.

7. Shui, M.; Yue, L.; Liu Q.; Xu. Z. Chinese Journal of Inorganic Chemistry **1999**, *15*, 715.
8. Sadtler Commercial Spectra IR Grating Inorganics, Vol. 1, No. y41k.
9. Rao, C.N.R. In *Chemical Applications of Infrared Spectroscopy*; Academic Press, 1963; 23.
10. Louisfert, J.C.R. Hebd. Seanc.; Acad. Sci.: Paris, **1959**; *248*, 1150.
11. Donoghue, M.; Hepburn, P.H.; Ross, S.D. Spectrochim. Acta, Part A **1971**, *27*, 1065.

Received November 25, 2000
Accepted July 18, 2001