BRIEF COMMUNICATION

Raman Study of Prereactional Transformations in Calcium Hydroxide Crystals during a Thermal Treatment Leading to Dehydration

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The Raman spectroscopy study of $Ca(OH)_2$ single crystals shows that important modifications take place in the crystal structure far below the dehydration temperature. In particular, an intense and broad background scattering and a broad band centered at ~1650 cm^{-1} evolve in the Raman spectra.

Introduction

The decomposition reaction of brucite type hydroxides involves three successive reaction steps: (a) formation of water molecules from hydroxyl ions, (b) water elimination out of the solid, and (c) structural transformation from the hydroxide to the oxide structure.

A previous X-ray and neutron diffraction study (1) has shown that, prior to the decomposition, the hydroxide undergoes slight structural changes which are probably linked to the formation and non-uniform distribution of H_2O molecules on OH^- lattice sites. This result is in agreement with earlier studies by Freund and co-workers (2–4), using proton conductivity techniques.

The aim of this work is to use Raman spectroscopy to get additional information about these prereactional modifications, mainly from a dynamical point of view. We only give here the first experimental results.

Experimental

$Ca(OH)_2$ single crystals are prepared under vacuum with the Ashton and Wilson

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method (5) by slow diffusion of a calcium chloride solution into a potassium hydroxide solution. They are transparent straight prisms of hexagonal section. Their sizes vary from a few tenths to 1 or 2 mm.

The spectrometer is a SPEX 1301 double monochromator. The crystal is illuminated by the 5145-Å line of a SPECTRA PHYSICS 164 argon laser. The Raman scattered light is detected by a photomultiplier HAMAMATSU connected to a photon counting system PAR 1110.

The $Ca(OH)_2$ single crystal is heated in a vertical, cylindrical furnace. The sample holder is fixed at the end of an axial rod which contains a thermocouple and is heated by the thermal radiation of a "Thermocoax" resistance. Three windows, at right angles, allow the incident and diffused beams to go in and out of the furnace. The fourth direction is connected to a vacuum system and a pressure gauge.

All experiments were performed under vacuum (10^{-4} Torr). During each experiment, a $Ca(OH)_2$ crystal was gradually heated from room temperature to its decomposition temperature. *Each experiment was carried out with a new crystal.* Thus the temperatures at which the different transformations occurred, varied from one experiment to another. It is to be noted that, due to the laser irradiation, the temperature of the diffusing area of the crystal may be 20 to 30°C higher than the temperature measured at the crystal surface.

The Raman spectra were recorded at constant temperature with a laser power of 150 mW, the beam being focussed on the sample. The spectrometer slits were set at 250 μm corresponding to a resolution of 7.8 cm^{-1}.

Results and Discussion

$Ca(OH)_2$ crystallizes with a CdI_2 type structure in the $P\bar{3}m1$ spatial group (6–11). Its Raman spectrum exhibits four lines belonging to the symmetry classes E_g, A_{1g},

E_g, and A_{1g}. The first three lines observed at 252, 355, and 675 cm^{-1} at room temperature correspond to two translational and one rotational modes of the OH^- against the cations, the fourth line at 3615 cm^{-1} corresponds to the internal vibration of the O–H bond. The CaO oxide, which is formed in the decomposition, is Raman-inactive. The crystal decomposition occurs between 180 and 200°C (depending on the sample). This decomposition is attested by the disappearance of all Raman lines due to the formation of Raman-inactive oxide.

A typical evolution of the spectra is shown in Fig. 1. All spectra plotted in this figure have been recorded with the same crystal at different temperatures except for the spectrum marked by a star ($T^* = 155°C$) which was taken on another sample. We have incorporated it into Fig. 1 in order to make the spectrum evolution more evident. The most interesting information appears to lie in the evolution of the background intensity with temperature. We denote by background intensity, the intensity of the light which is not associated with Raman lines.

Between ambient and the beginning of the thermal treatment ($T < 152°C$), the background intensity increases very slightly. Then a very broad band evolves with a maximum situated around 1650 cm^{-1} ($T = 152°C$ and $T^* = 155°C$). This band could be attributed to the bending mode of the H_2O molecules. In this case, it would indicate that H_2O molecules form inside the crystal while the hydroxide structure still persists as evidenced by the characteristic Raman lines of $Ca(OH)_2$ in the spectrum. Similar observations of formation of H_2O in $Mg(OH)_2$ detected by ir spectroscopy, are reported by Wengeler *et al.* (3).

Simultaneously, or at a temperature a few degrees higher (157°C), depending on the crystal, the background intensity increases abruptly. The background increase is highest at low frequencies and decreases as the frequency increases. Above 157°C the background level further increases
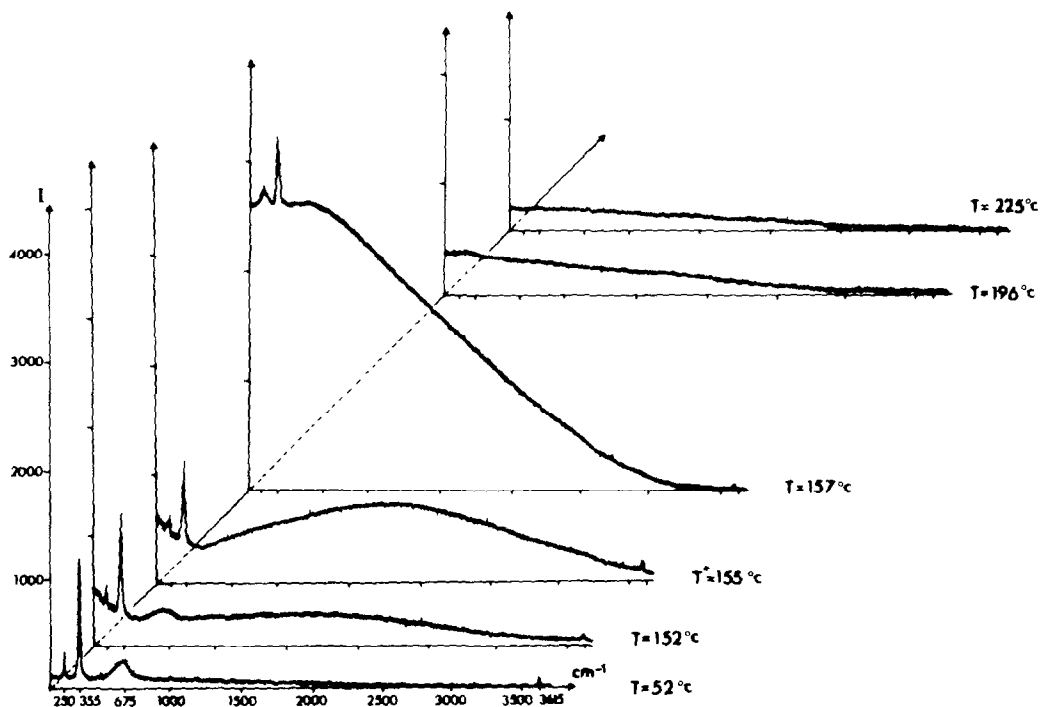
FIG. 1. General evolution of the Ca(OH)$_2$ Raman spectra with temperature. (*) This spectrum is issued from another experiment in which the broad band appears more distinctly.

slightly and then decreases toward 196°C. At 225°C it has returned to a low value close to its room temperature value. At temperatures above 225°C there is no further change. The reason for the sharp increase in the background intensity is not obvious.

After dehydration the outer shape of the Ca(OH)$_2$ crystal is preserved but it then consists of a rather fragile assembly of oxide microcrystallites well oriented with respect to each other and to the parent hydroxide crystal (*12*). Such a polycrystalline sample is responsible for a large static diffusion of the incident laser beam (elastic scattering without frequency shift). However, this static diffusion is not responsible for the observed background intensity increase: no static diffusion can explain the fact that the background intensity increase extends as far as 3000 cm^{-1} from the central line. Moreover, it is noted from Fig. 1 that

the high background decreases again toward 225°C while the elastic scattering of the central line remains high due to the smallness of the CaO crystallites.

Thus the sharp increase in the background intensity around 157°C could arise from a dynamical contribution to the diffusion of the laser light coming from fast and large amplitude motions in the crystal (*13*). Protons could be involved in these motions.

The proton conductivity studies by Freund *et al.* (*2–4*) indicate that mobile protons exist in the hydroxide structure before the onset of the dehydration. Yet some other observations provide evidence for a modification of the bonding state of the protons prior to the onset of the dehydration. The results obtained by X-ray and neutron diffraction (*1*) in the case of Ca(OD)$_2$ show that the deuterium positions seem no longer well defined above a certain temperature which lies several ten degrees below the de-

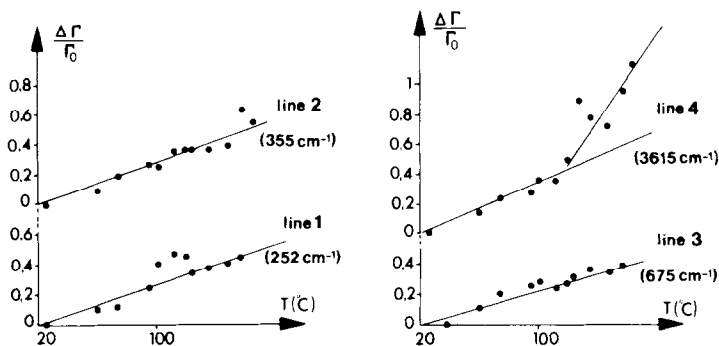FIG. 2. Relative broadenings at half-maximum $\Delta\Gamma/\Gamma_0$. $\Delta\Gamma = \Gamma - \Gamma_0$, Γ = width at T°C, Γ_0 = width at $T_0 = 38$°C.

composition temperature. The comparison of the Raman linewidths in our experiments at different temperatures provides further support. The relative broadening versus temperature for the four lines is reported in Fig. 2. The fourth line (3615 cm^{-1}), corresponding to the OH ion internal mode, exhibits a broadening, from a temperature about 110°C, which is almost three times higher than the three related to translational and rotational lattice modes. This is unusual since internal modes are generally much less temperature-dependent than the external ones (14).

Thus, the present results corroborate the already mentioned phenomenon (1–4): various modifications occur in the calcium hydroxide structure several ten degrees below the decomposition temperature. We cannot at present give a complete and coherent interpretation of the modifications described here. Further experiments are now in progress. All the results will be discussed in a following paper.

Acknowledgments

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