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BRIEF COMMUNICATIONS

Evidence of a Luminescence Band during the Thermal Transformation of Calcium Hydroxide

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New Raman spectroscopy results are available. The broad band occurring in the Raman spectra of $Ca(OH)_2$ during a thermal treatment is not a Raman line but supports a luminescence process. Some features of the luminescence band are given. © 1988 Academic Press, Inc.

Introduction

The temperature evolution of the Raman spectrum of $Ca(OH)_2$ during a thermal treatment leading to dehydration has been previously reported (*1*). The four Raman lines of $Ca(OH)_2$ observed in the spectrum are in perfect agreement with the assignments made earlier by several authors (*2*–*5*). However, the second-order Raman spectrum of CaO reported in other studies (*6*, *7*) was not observed in our case due to the finely divided state of the material resulting from the hydroxide dehydration. The main result issued from this study was the appearance of a broad band in the spectrum. As announced in a recent paper (*8*), further Raman results are now available. They are reported in the present paper and lead to a new identification of this broad band.

Typical Temperature Evolution of the Raman Spectrum of $Ca(OH)_2$

Previous Raman spectra of a single crystal of $Ca(OH)_2$ recorded in vacuum at different temperatures using the 5145-Å line of an Argon laser exhibit a very broad band centered around 1650 cm^{-1} from a tempera-

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ture close to 152–155°C. The experimental details have been previously given (*1*).

Due to this particular shape of the spectra and to the very low intensity of the O–H line which was previously measured with other experimental equipment as an intense line, the response curve of the photomultiplier used in these experiments was registered. As shown in Fig. 1b, the curve is continuously decreasing in the frequency range of the spectra. Therefore, the spectra, and particularly the shape and the frequency shift of the band, were directly affected by the lack of efficiency of the photomultiplier in this domain.

Later, the Raman spectra of single crystals and polycrystalline samples of $Ca(OH)_2$ were recorded also in vacuum and with the same exciting line (λ = 5145 Å) but using other spectrometers (Coderg LRDH 800 and Dilor RTI 30) and photomultipliers (RCA C31034 and RCA 3034), having their maximum efficiency in the frequency range of the spectra (Fig. 1a). These spectra exhibited the same evolution of a very broad band (Fig. 2). However, the band is shifted to higher frequencies: around 2600–3200 cm^{-1} (Fig. 2) instead of 1650 cm^{-1} (Fig. 1 in Ref. (*1*)). The Raman line corresponding to the stretching O–H mode (3618 cm^{-1}) becomes the more intense line of the spectrum in contrast with the former records. No anomaly is noticed about the temperature evolution of the Raman lines. In particular, the four lines undergo the same broadening with increasing temperatures.

The main result drawn from the whole Raman experiments mentioned above is the development of a broad band in the spectra. However, it cannot be attributed to the bending mode of H_2O molecules, as suggested in (*1*).

Nature of the Band

In order to characterize the broad band, both the Stokes and anti-Stokes spectra of a $Ca(OH)_2$ single crystal were recorded and several exciting lines with different wavelengths (4880, 5145, 5682, and 6471 Å) were used.

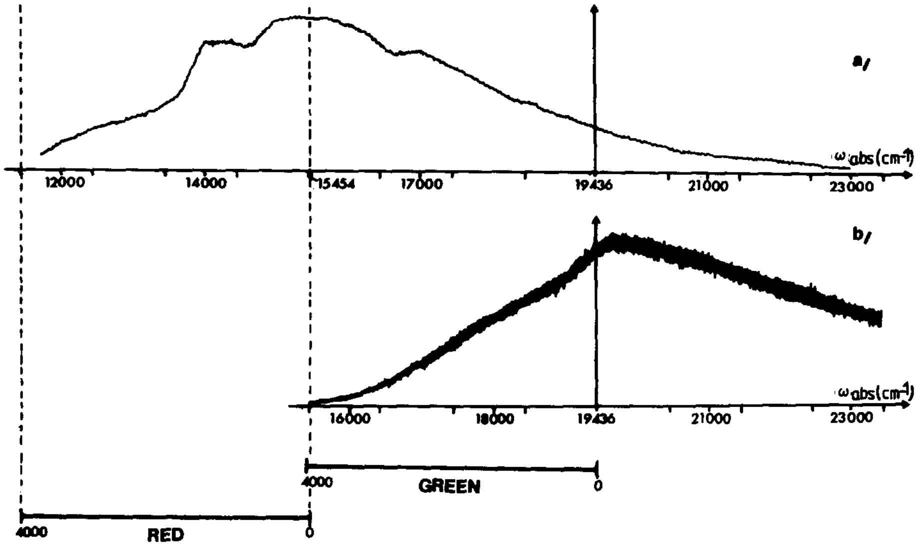

FIG. 1. Response curves of the RCA C31034(a) and Hamamatsu (b) photomultipliers used with the Coderg LRDH 800 and Spex 1301 spectrometers, respectively. The response of the RCA 3034 photomultiplier used with the Dilor RTI 30 spectrometer is (a) type.

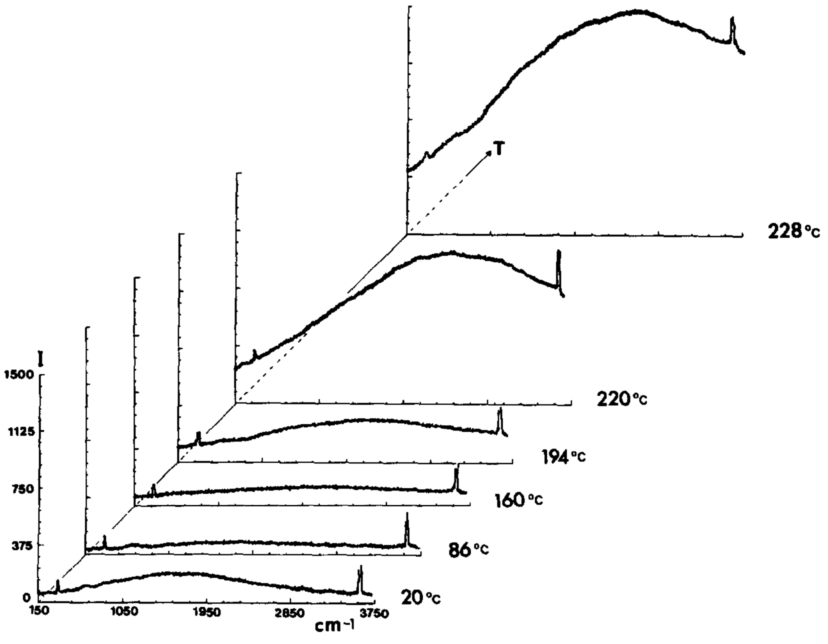

FIG. 2. Temperature evolution of the Raman spectrum of $Ca(OH)_2$ (λ = 5145 Å, Coderg LRDH 800 spectrometer).

The broad band only covers the Stokes domain but is not present in the anti-Stokes one. Moreover, its frequency shift ω_{max} depends upon the incident wavelength (Table I). Both these results attest that the band is not a Raman line but supports a luminescence process. Indeed, the domain of absolute frequency corresponding to the maximum of the band is the same whatever the incident wavelength may be (4880, 5145 and 5682 Å, Table I). With the fourth exciting line (λ = 6471 Å), the excited energy level from which the luminescence occurs is lower than the level reached with the other three lines (ω_{abs} = 16,500 cm^{-1}) because the value of the incident frequency ω_0 = 15,454 cm^{-1} is lower than this energy level. Moreover, the spectra are strongly affected by the lack of efficiency of the photomultipliers in the red spectral domain (see Fig. 1). Thereby, the experimental values of the frequency shift ω_{max} and of the absolute frequency ω_{abs} of the band are not certain and are given between parentheses in Table I.

The width of the luminescence band does not depend upon the wavelength: the full width at half maximum is about 3400 cm^{-1} in the temperature range between 130 and 230°C. The averaged lifetime of the related excited state is close to 10^{-14} sec. At higher temperatures, the band width seems to be larger, about 4500 cm^{-1} at 800°C. The temperature evolution of the band intensity is

TABLE I

VARIATION OF THE FREQUENCY SHIFT ω_{max} AND OF THE ABSOLUTE FREQUENCY ω_{abs} OF THE MAXIMUM OF THE BROAD BAND FOR DIFFERENT EXCITING LINES (FREQUENCY ω_0)

λ (Å)	ω_0 (cm^{-1})	ω_{max} (cm^{-1})	ω_{abs} (cm^{-1})
4880	20492	3800–4300	16692–16192
5145	19436	2600–3300	16836–16136
5682	17599	~1450	16149
6471	15454	~(800–1000)	(14654–14454)

no more dependent upon the wavelength. The intensity suddenly increases at about 200°C for polycrystalline samples and at about 150°C in the case of single crystals. For higher temperatures, the band intensity further increases or remains high but never decreases if the thermal treatment is performed under vacuum.

Thus, the Raman study carried out during a thermal treatment of $Ca(OH)_2$ provides evidence of a luminescence process in such samples. Possible causes of the luminescence, and also the relation between this luminescence and the decomposition reaction itself, are detailed elsewhere (*9*).

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