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Comment on the Raman Study of the Thermal Transformation of Calcium Hydroxide

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The interpretation of a recent Raman study of the thermal transformation of $Ca(OH)_2$ by Chaix-Pluchery *et al.* (*J. Solid State Chem.* **53**, 273, 1984), is questioned since it it based on the erroneous assumption that CaO is Raman-inactive.

In a recent paper in this journal, Chaix-Pluchery *et al.* (*1*) have reported on a Raman study of the thermal treatment of a $Ca(OH)_2$ crystal. Since no lines in the Raman spectra were observed above about 200°C in their study, the authors of Ref. (*1*) concluded that $Ca(OH)_2$ has converted to CaO since "CaO is Raman-inactive." The purpose of this note is to point out that although CaO has no first-order Raman effect, a second-order Raman effect involving the scattering of two phonons is observed in CaO (*2, 3*) and in other materials with rock salt structure (*4*). Despite the fact that two phonons are involved in the second-order effect, the Raman spectrum of CaO shows fairly sharp bands near 530 and 660 cm^{-1} and a broader band near 1000 cm^{-1} (*2, 3*). This fact, combined with several unexplained features of the observations in Ref. (*1*) point to the need for a more careful study of the thermal treatment of $Ca(OH)_2$.

Some of the major observations of Ref. (*1*) are as follows. At room temperature, the Raman spectra of $Ca(OH)_2$ in Ref. (*1*) consists of four bands at 252, 355, 675, and 3615 cm^{-1}. This is in agreement with the Raman study of $Ca(OH)_2$ by another group (*5*), although Ref. (*5*) shows a considerable structure (satellites) to the 3615-cm^{-1} band. As the temperature of the crystal is raised to 155°C, a very broad band centered around 1650 cm^{-1} is observed in Ref. (*1*), in addition to the bands at 252 and 355 cm^{-1} (the band at 675 cm^{-1} is no longer observed, probably due to the large background of the 1650-cm^{-1} band). At 157°C, the intensity of the broad band increases enormously and it shifts to lower energies whereas the bands near 252 and 355 cm^{-1} are still observed. For higher temperatures (196 and 225°C) the intensity of the background band decreases as temperature increases and bands at 252 and 355 cm^{-1} corresponding to $Ca(OH)_2$ are no longer observed. It is at this stage that authors of Ref. (*1*) conclude that CaO is formed since no Raman lines are observed.

Considering that CaO is not Raman-inactive as noted earlier and that the nature of the broad band observed in Ref. (*1*) is still uncertain, the interpretation of the observa-

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tions in Ref. (*1*) requires a careful reexamination. If the broad band is due to CaO formed, corresponding to the 1000-cm^{-1} band of CaO (*2, 3*), then why are not the bands near 530 and 660 cm^{-1} observed in the experiments of Ref. (*1*)? If CaO is present and signal to noise is not a problem, then bands due to CaO should have been observed in Ref. (*1*). The nature of the broad band and its shift with temperature is also not understood. Temperature-dependent changes in the structure of $Ca(OH)_2$ are presumably responsible for this band (for example, Marks *et al.* (*6*) have reported on a band near 1200 cm^{-1} due to O_2^- in $Ca(OH)_2$). However, based on the reported observations of Ref. (*1*) and the known Raman spectra of CaO, it may be concluded that either CaO is not the final product of the thermal transformation of $Ca(OH)_2$ in the experiments of Ref. (*1*) or the signal to noise of the experiment is not sufficient to detect CaO. In either case a more careful Raman study of the thermal transformation of $Ca(OH)_2$ is warranted.

References

1. O. Chaix-Pluchery, D. Ciosmak, J. C. Niepce, and M. Peyrard, *J. Solid State Chem.* **53,** 273 (1984).
2. M. Voisin and J. P. Mon, *Phys. Status Solidi B* **48,** K185 (1971).
3. K. H. Reider, B. A. Weinstein, M. Cardona, and H. Bilz, *Phys. Rev. B* **8,** 4780 (1973).
4. R. Loudon, *Adv. Phys.* **13,** 423 (1964).
5. T. Stanek and G. Pytasz, *Acta Phys. Pol. A* **52,** 119 (1977).
6. J. Marks, W. Wencheback, and N. J. Poulis, *J. Phys. C* **13,** 5481 (1980).