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Discussion

A reply to the discussion by Lucia Fernández-Carrasco

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1. Introduction

The discussion of the work of Kutty and Nayak [1] by Fernández-Carrasco [2] is very useful. Fernández-Carrasco discusses the application of infrared (IR) absorption spectroscopy in the study of barium orthoaluminate hydrates. The main theme of the discussion is the assignment of 1440 cm^{-1} absorption band by us to Al-OH-Al stretching vibrations, which according to the author is due to CO_3^{2-} group.

2. Reply

The CO_3^{2-} ion in a D_3 or D_{3h} site symmetry shows three IR absorption bands in the regions 1530–1320 cm^{-1}, 860–800 and 760–670 cm^{-1}, corresponding to three normal modes of vibration: asymmetric stretching (ν_3), symmetric bending (ν_2), and asymmetric bending (ν_4) vibrations [3]. The totally symmetric stretching (ν_1) vibration is usually not IR active. The ν_3 and ν_4 vibrations are degenerate in these high symmetry groups; as a result, only three bands can be observed in the IR spectrum. As the site symmetry reduces, for example for C_{2V} or C_S, the degeneracy of ν_3 and ν_4 vibrations will be lifted and each will split into doublets [3]. In addition, the symmetric stretching vibration is also active in this low site symmetry and appears as a weak, sharp absorption band in the IR spectrum. This indicates that CO_3^{2-} shows multiple absorption bands in the spectrum. Hence, the presence of single strong absorption band at 1440 cm^{-1} is not sufficient to conclude the presence of CO_3^{2-} species in the compound.

The above discussion can be further substantiated by comparing the IR spectrum of $BaCO_3$ and hydrated barium orthoaluminates as shown in Fig. 1(*a*) and (*b*). X-ray diffraction shows $BaCO_3$ as the second phase on exposure of barium orthoaluminate hydrate to CO_2-containing atmosphere. The spectrum of $BaCO_3$ shows multiple absorption bands and also shows the overtones. The assignments of these bands are done based on the above discussion. This indicates that, ν_1, ν_2, and ν_4 absorption bands cannot be ignored when identifying CO_3^{2-} species in an unknown sample. These bands are not present in the spectrum of barium orthoaluminate hydrate sample, as shown in Fig. 1(*b*), which leads us not to assign the 1440 cm^{-1} band in the barium orthoaluminate hydrate spectrum to ν_3 vibration of CO_3^{2-} group. It is significant to mention that the samples deliberately exposed to CO_2 atmosphere showed all the CO_3^{2-} absorption bands in the spectrum.

References

[1] T.R.N. Kutty, M. Nayak, Cem Concr Res 28 (10) (1998) 1393–1404.
[2] L. Fernández-Carrasco, Cem Concr Res 29 (10) (1999) 1697–1698.
[3] K. Nakamato, Infrared Spectra of Inorganic and Coordination Compounds, John Wiley & Sons Inc., New York, 1963.

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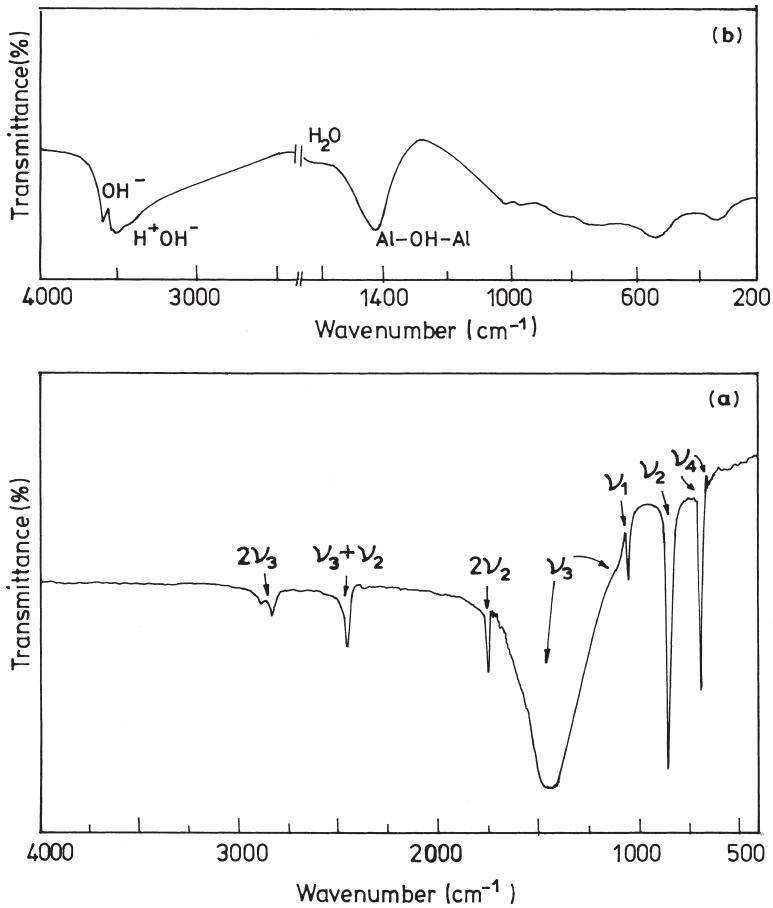

Fig. 1. IR spectra of (*a*) $BaCO_3$ and (*b*) $Ba_{0.76}Al_2(OH)_{7.52} \cdot H_2O$.