

## **Infrared and Raman study of interlayer anions $\text{CO}_3^{2-}$ , $\text{NO}_3^-$ , $\text{SO}_4^{2-}$ and $\text{ClO}_4^-$ in Mg/Al-hydroxalcalite**

**J. THEO KLOPROGGE,\* DAVID WHARTON, LEISEL HICKEY, AND RAY L. FROST**

Centre for Instrumental and Developmental Chemistry, Queensland University of Technology, 2 George Street, GPO Box 2434, Brisbane Qld 4001, Australia

### **ABSTRACT**

The difference in the local environment of  $\text{CO}_3^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{ClO}_4^-$  in Mg/Al-hydroxalcalite compared to the free anions was studied by infrared and Raman spectroscopy. In comparison to free  $\text{CO}_3^{2-}$  a shift toward lower wavenumbers was observed. A band around 3000–3200  $\text{cm}^{-1}$  has been attributed to the bridging mode  $\text{H}_2\text{O}-\text{CO}_3^{2-}$ . The IR spectrum of  $\text{CO}_3^{2-}$  hydroxalcalite clearly shows the split  $\nu_3$  band around 1365 and 1400  $\text{cm}^{-1}$  together with weak  $\nu_2$  and  $\nu_4$  modes around 870 and 667  $\text{cm}^{-1}$ . The  $\nu_1$  mode is activated and observed as a weak band around 1012  $\text{cm}^{-1}$ . The Raman spectrum shows a strong  $\nu_1$  band at 1053  $\text{cm}^{-1}$  plus weak  $\nu_3$  and  $\nu_4$  modes around 1403 and 695  $\text{cm}^{-1}$ . The symmetry of the carbonate anions is lowered from  $D_{3h}$  to  $C_{2v}$ , resulting in activation of the IR inactive  $\nu_1$  mode around 1050–1060  $\text{cm}^{-1}$ . In addition, the  $\nu_3$  shows a splitting of 30–60  $\text{cm}^{-1}$ . Although  $\text{NO}_3^-$ -hydroxalcalite has incorporated some  $\text{CO}_3^{2-}$  the IR shows a strong  $\nu_3$  mode at 1360  $\text{cm}^{-1}$  with a weak band at 827  $\text{cm}^{-1}$ , and the  $\nu_4$  band is observed at 667  $\text{cm}^{-1}$ , although it is largely obscured by the hydroxalcalite lattice modes. The Raman spectrum shows a strong  $\nu_1$  mode at 1044  $\text{cm}^{-1}$  with a weaker  $\nu_4$  band at 712  $\text{cm}^{-1}$ . The  $\nu_3$  mode at 1355  $\text{cm}^{-1}$  is obscured by a broad band due to the presence of  $\text{CO}_3^{2-}$ . The symmetry of  $\text{NO}_3^-$  did not change when incorporated in hydroxalcalite. The IR spectrum of  $\text{SO}_4^{2-}$ -hydroxalcalite shows a strong  $\nu_3$  at 1126,  $\nu_4$  at 614 and a weak  $\nu_1$  mode at 981  $\text{cm}^{-1}$ . The Raman spectrum is characterized by a strong  $\nu_1$  mode at 982  $\text{cm}^{-1}$  plus medium  $\nu_2$  and  $\nu_4$  bands at 453 and 611  $\text{cm}^{-1}$ ;  $\nu_3$  cannot be identified as a separate band, although a broad band can be seen around 1134  $\text{cm}^{-1}$ . The site symmetry of  $\text{SO}_4^{2-}$  is lowered from  $T_d$  to  $C_{2v}$ . The distortion of  $\text{ClO}_4^-$  in the interlayer of hydroxalcalite is reflected in the IR spectrum with both  $\nu_3$  and  $\nu_4$  bands split around 1096 and 1145  $\text{cm}^{-1}$  and 626 and 635  $\text{cm}^{-1}$ , respectively. A weak  $\nu_1$  band is observed at 935  $\text{cm}^{-1}$ . The Raman spectrum shows a strong  $\nu_1$  mode at 936  $\text{cm}^{-1}$  plus  $\nu_2$  and  $\nu_4$  bands at 461 and 626  $\text{cm}^{-1}$ , respectively. A  $\nu_3$  mode cannot be clearly recognized, but a broad band is visible around 1110  $\text{cm}^{-1}$ . These data indicate a lowering of symmetry from  $T_d$  to  $C_s$ .