

Raman spectroscopic studies of O–H stretching vibration in Mn-rich apatites: A structural approach

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ABSTRACT

The O–H stretching vibration mode in crystals of (Mn,Cl)-rich and F-poor minerals of the apatite-supergroup has been studied by micro-Raman spectroscopy. The main purpose was to check if such an analysis can provide a quick and simple method to assess the distribution of Ca and Mn together with traces of Fe + Mg (= Mn*) on nonequivalent cationic sites in the apatite structure, especially in small and strongly heterogeneous crystals directly in thin sections. The O–H stretching vibration mode can then be treated as a useful structural probe giving information on the M2 occupants bonded to ^XOH. Pieczkaite, with the empirical formula (Mn_{4.49}Fe_{0.47}Ca_{0.05}Mg_{0.01})_{Σ5.01}P_{2.99}O₁₂[Cl_{0.83}(OH)_{0.17}], displays the O–H stretching mode centered at ~3380 cm⁻¹, which shows that the complete replacement of Ca by Mn* at the M2 site is connected with a shift of the O–H stretching band ~192 cm⁻¹ toward lower wavenumbers in relation to the O–H Raman band position reported for hydroxylapatite. The value is high enough to be an indicator of the ^{M2}Mn*···OH content in any sample of Mn-enriched apatite. Studies of the fine structure of the band disclosed its dependence on (1) the local combinations of Ca and Mn* forming triplets of M2 cations bonded to the X anion, (2) the presence of OH+Cl at the two half-occupied X sites that form chemical bonds with the M2 cations varying in strength and length, and (3) the spatial geometry of the X–M2 bonds and polarizability of the monovalent X anion by varying cations in the M2M2M2 triplets. The deconvolution of the band into maximum eight component bands with constant Raman shifts opens the possibility of evaluating the averaged M2M2M2 triplet bonded to oxygen of the ^XOH group. If the OH/(OH+Cl) fraction is known, the amounts of Ca and Mn* bonded to ^XOH can also be estimated. Application of the method to the holotype parafiniukite showed a slightly different distribution of Ca in M2M2M2 triplets than had been assumed from single-crystal X-ray diffraction. However, it corroborates suggestions that in the apatite structure there may be a preference for ^{M2}Ca to be bonded to ^XOH and ^{M2}Mn* to ^XCl. Our results show that the proposed method can be used as an independent tool in structural studies of Mn-rich minerals of the apatite-supergroup, providing results complementary to single-crystal X-ray diffraction. This method can easily be adjusted to modern apatite-type nanomaterials synthesized for biomedical and various industrial applications.

Keywords: Mn-bearing minerals of the apatite supergroup, Raman spectroscopy, O–H stretching vibration, pieczkaite, parafiniukite