POLARIZED INFRARED STUDY OF SINGLE CRYSTALS OF APATITES[1]

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Since the use of the KBr pellet technique is of limited value for the assignment of the bands in the spectra of the apatites, it became necesssary to study single crystals with polarized IR reflectance techniques. This technique can give additional information on the orientation of the groups and the directions of their various transition moments and thus allows the assignment of the bands.

The positions of the bands in the reflectance spectra are comparable to those in the absorption spectra. However, in the reflectance spectra, the intensities vary considerably with the orientation of the crystal, being maximal in a certain position and minimal in a position 90° to it. In the reflection from the (100) face of an F-apatite crystal, the ν_4 band looks like a single degenerate strong band at 575 cm^{-1} when the c-axis of the crystal is aligned parallel to the E-vector of the IR beam. After turning the crystal so that the c-axis is perpendicular to the E-vector, a peak at 605 cm^{-1} has appeared with a high intensity while the 575 band is reduced. Reflection from the (001) face shows the 605 peak at its maximum. In addition, the ν_1 band is maximal and a new band is detected at 1125 cm^{-1}. Tilting the crystal to obtain the reflection from the (111) face presents the ν_4 band as a definite triplet with 3 distinct peaks at 610, 588, and 575 cm^{-1}. This establishes that the 588 peak (which has been observed as a shoulder in the absorption spectrum) is definitely a member of the ν_4 mode and the band at 1125 cm^{-1} (not observed in the absorption spectrum) is a member of the ν_3 mode of the PO_4 group.

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CARBONATE SUBSTITUTION IN THE APATITE STRUCTURE[1]

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The carbonate in the carbonate-containing apatites has been proposed to be either adsorbed on the surface of the apatite crystallites or to be within the apatite structure, substituting either for OH or for PO_4 groups.

In the present study of a series of CO_3OH^- and CO_3F^- apatites prepared for aqueous solutions, the length of the a-axis has been found to decrease proportionally to the increase in the carbonate content of the precipitate. The a-axis contraction with carbonate inclusion indicates that the planar CO_3 group is substituting for the larger tetrahedral PO_4 group.[2] The IR absorption spectra of these precipitates are similar to the spectra of the various carbonate-containing mineral apatites (dahllite, francolite).

Synthetic carbonate apatites prepared at high temperature by passing dry CO_2 over OH-apatite show an expansion of the a-axis, indicating a CO_3 for OH substitution.[3] Their IR spectra differ from those of the mineral apatites.

We consider, therefore, that in the mineral apatites the carbonate substitutes for the phosphate groups and not for the OH groups.

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[2] LeGeros, R. Z. (1965), *Nature* 206: 403; (1967), Ph.D. Thesis (New York University).
[3] Elliott, J. C. (1964). Ph.D. Thesis, University of London.