The infrared spectrum of synthetic akaganéite, $\beta$-FeOOH

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ABSTRACT

Fourier-transform infrared spectra of a synthetic akaganéite, $\beta$-FeOOH, were acquired in transmittance, attenuated total reflectance (ATR) and diffuse reflectance. The transmittance spectra showed a distinct dependence on the mode of sample preparation: measurements taken on pellets prepared by pressing the sample with alkali halides (KBr or CsI) displayed bands at 1096, 1050, and 698 cm$^{-1}$ that were not observed in spectra of the neat material and must therefore be considered artifacts. Variations in the sampling environment (e.g., water and/or organic volatiles) were also observed to exert a noticeable influence on the development of the IR spectra.

Infrared bands due to akaganéite were found at 3480 + 3390 (doublet), 1630, 850 + 820 (doublet), 650, 490, and $\sim$420 cm$^{-1}$. Diffuse reflectance spectra dominated by volume scattering (loose), diffuse reflectance spectra comprised of both volume and surface scattering (compacted), ATR spectra (surface only), and transmittance spectra (absorbance only, inverse of ATR) showed compatible trends for the akaganéite features both above and below $\sim$1000 cm$^{-1}$. This indicates that the multiple akaganéite measurements are consistent and confirms the band assignments.

INTRODUCTION

Akaganéite, nominally $\beta$-FeOOH, is rare in nature. Numerous papers have nevertheless been occupied with this mineral and its synthetic analogs. Alleged common occurrences of akaganéite in soils based on early Mössbauer spectroscopy work were not confirmed by other methods. Later studies showed such claims to result from misinterpretations of equivocal data, and attempts to identify akaganéite on the basis of Mössbauer spectra, especially when these have been taken in the paramagnetic state, must invariably be questioned.

The formation of akaganéite is known to require the presence of either Cl or F ions, and therefore the formula should be given as FeO(OH)$_x$Cl$_{1-x}$ or FeO(OH)$_x$F$_{1-x}$, respectively. The necessity for the presence of Cl or F explains the scarcity of akaganéite in nature. Confirmed occurrences of akaganéite have been typically reported from Fe- and Cl-rich environments such as hydrothermal brines (e.g., Holm et al. 1983) and as a result of corrosion in the presence of chloride (e.g., Keller 1970; Taylor et al. 1974). Chemical analyses of natural akaganéites have revealed significant variations in both cation and anion composition. Examples for such substitutions are a partial replacement of Fe by Ni (Post and Buchwald 1991) or a complete replacement of chloride by tungstate, WO$_4^{2-}$ (Walenta 1982), the latter thus possibly qualifying as a separate mineral species.

Akaganéite usually occurs in so-called somatoids, spindle-shaped crystals about 0.2–0.5 $\mu$m long and 0.02–0.1 $\mu$m wide. Early electron microscopy data was taken to indicate the presence of 3 nm $\times$ 3 nm large hollows in the structure (Watson et al. 1962; Gallagher 1970), but subsequent work showed this to be an artifact due to dehydroxylation under the electron beam (Galbraith et al. 1979). Akaganéite is isostructural with hollandite, Ba(Mn$^{4+}$,Mn$^{2+}$)$_8$O$_{16}$, and schwertmannite, Fe$_8$O$_8$(OH)$_6$SO$_4$; its structure thus has 0.5 nm $\times$ 0.5 nm wide tunnels in which the halogens are located running parallel to the c axis (not to be confused with the conjectural hollows mentioned above). However, even basic structural particulars such as the space group have been open to discussion until recent years (Post and Buchwald 1991).

Interactions between the halogens and neighboring Fe$^{3+}$ ions are considered to be responsible for the development of relatively complex Mössbauer spectra both in paramagnetic and magnetically ordered akaganéite (e.g., Murad 1979; Childs et al. 1980). On the basis of room-temperature Mössbauer spectra, Mulaba-Bafubiandi et al. (1990) inferred the possibility of an exchange of anions in the tunnels, although such an exchange is probably only partial (Ellis et al. 1976). Extensive ion-exchange phenomena have also been observed in schwertmannite (Murad et al. 1994), rendering this and related phases of potential interest as ion-exchange materials and hydrocracking catalysts for coal liquefaction (Linehan et al. 1977).

A smattering of papers concerned with akaganéite has provided IR data, but band assignments were made in only few of these. Müller (1967) described the synthesis and properties of a variety of Fe oxyhydroxides, among which two precipitates were alleged to be modifications of $\beta$-FeOOH. The preparation of these (named $\beta_1$-FeOOH and $\beta_2$-FeOOH), however, in-