Far-infrared spectra of ammonium layer and framework silicates

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Abstract

The low-temperature behaviour of the ammonium mica: synthetic ND$_4$-tobelite and ND$_4$-phlogopite has been studied by infrared spectroscopy in the far infrared region, from room temperature down to 20 K. Unlike previously studied low-temperature, orientational ordering of the ammonium ion in the interlayer region from the near infrared region (Mookherjee et al., 2002a,b), the bands in far infrared region do not show significant change on cooling. This indicates that the coupling between ordering of ammonium ions and other structural rearrangements is weak.

Key words: Ammonium, low-temperature, far-infrared spectroscopy, mica.

Introduction

The use of far infrared (FIR) spectroscopy in mineralogy has developed in parallel strands. In part, FIR studies of clay minerals have been driven by the potential of FIR as an indicator of planetary mineralogy in remote sensing applications, starting with lunar exploration and continued to this day in studies of the rocky bodies of the Solar system (Gawarecki et al., 1969; Clegg et al., 1972; Perry et al., 1972; Pugh and Bastin, 1975; Vickers and Bastin, 1977; Ward et al., 1977; Courtin et al., 1979). But it is also clear that the application of FIR spectroscopy to the study of alkali cations in clays minerals has enhanced our understanding of the environment of the compensating cation. In particular, details of the alkali ion bonding into the tetrahedral layer, as well as perturbations due to tetrahedral rotations and distortions,
have been seen to be expressed as changes in the details of the FIR signal (Ishii et al., 1969; Tateyama et al., 1977; Fripiat, 1981; Velde and Couty, 1985; Prost and Laperche, 1988; Schroeder, 1988; Prost and Laperche, 1990; Laperche and Prost, 1991; Schroeder, 1991; Harsh et al., 1992; Schroeder, 1992; Liu, 1996; Diaz et al., 2000, 2002a,b; Boukili et al., 2001; Badreddine et al., 2002a,b). These investigations have shown that the strong clay-cation interactions in clay interlayers gives rise to characteristic FIR absorption features. The most recent data (Diaz et al., 2002a,b), for example, have allowed the building of a model in which large cations are seen to "wedge open" the expandable interlayer of the vermiculite structure. Examples of the use of FIR to study framework silicates, including the nature of the alkali cation within them, include the work of Angino (1968, 1969), Ishii et al. (1971), Wyncke et al. (1981), and Paluszkiewicz and Zabinski (1992).

Here we extend these earlier studies and report the far infrared spectra of synthetic deuterated ammonium muscovite (ND$_4$-tobelite: Harlov et al. 2001a) and deuterated ammonium phlogopite (Harlov et al. 2001b). We compare these with the FIR absorption of an ammonium-free dioctahedral phengite $2M_1$ (Mookherjee et al., 2001). Finally, far-infrared spectra have also been obtained for synthetic ND$_4$-buddingtonite (a framework silicate) and these are compared with previously-observed data for disordered alkali feldspar.

**Materials and Experimental Method**

**Sample Preparation:**

Ammonium silicates namely ND$_4$-tobelite, ND$_4$-phlogopite and ND$_4$-buddingtonite were synthesized as powders as outlined in Harlov et al. (2001a,b,c). Phengite $2M_1$ ($K_{0.95}Na_{0.05})(Al_{0.76}Fe_{0.14}Mg_{0.10})_2(Si_{3.25}Al_{0.75})O_{10}(OH_{1.96}F_{0.04})$ is a natural sample from
Greece, previously investigated by Mookherjee et al. (2001), Mookherjee and Redfern (2002).

**Infrared spectroscopy:**
For the powder absorption FIR spectra, a conventional pellet method was employed. Polythene was used as matrix. The sample matrix mixture was pressed into disc-shaped pellets of 13 mm diameter at room temperature under vacuum. Pellets weighed around 100 mg and contained a sample mass of around 2 mg. A Hg-arc source, DTGS detector, and Mylar 6µm beam splitter were used to record spectra in the wave number region from 50 to 700 cm⁻¹. Spectra were recorded over 1000 scans using a Bruker 113v instrument.

**Result and Discussion**
Diaz et al. (2002a,b) reported FIR spectra of (K, NH₄)-vermiculite and (NH₄, Cs)-vermiculite. They presented a series of spectra with varying (NH₄⁺/NH₄⁺+K⁺) and (NH₄⁺/NH₄⁺+Cs⁺) ratios. The potassium end member of the (K, NH₄)-vermiculite series shows a band due to the K-O stretch at 81 cm⁻¹. In contrast, the ammonium end member shows a band due to the NH₄⁺-O stretch at around 126 cm⁻¹. The occurrence of this band at a higher wave number is a result of the lower mass of NH₄⁺ compared to K⁺. In Fig. 1 we show three of our FIR spectra. ND₄-tobelite is a dioctahedral mica similar to muscovite except that ammonium occupies the interlayer site. The FIR spectrum for this sample shows a band at around 140 cm⁻¹ which we attribute to the ND₄⁺-O stretch. Similarly ND₄-phlogopite is a trioctahedral mica with ammonium in the interlayer. Its FIR spectrum shows a band at around 124 cm⁻¹, attributed to the ND₄⁺-O stretch, following the arguments of Diaz et al. (2002a).
Bands due to K-O stretching, which are present in phengite $2M_1$ are totally absent in the ammonium analogues. Conversely, bands due to the ND$_4^+$-O stretch are absent in phengite, as expected. These observations validate the band assignments and confirm the assumptions of Diaz et al. (2002a). The powder FIR spectrum for phengite $2M_1$ shows three peaks at around 94, 105 and 140 cm$^{-1}$ attributed to the transition moments parallel to the $b$, $a$, $c^*$ directions of the crystalline lattice (Diaz et al., 2000; Mookherjee and Redfern 2002).

For framework silicates, the FIR data are a little more complicated. Although assignments similar to those for the phyllosilicates are lacking, we may draw an analogy between the large interlayer counter-ions of micas and the large alkali site of the feldspar aluminosilicate framework, in order to assign the observed FIR bands. Figure 2 shows the FIR spectra of ND$_4$-buddingtonite collected at room temperature. For comparison a spectrum for an Al/Si disordered alkali feldspar is also shown. Broad bands from 300-500 cm$^{-1}$ give a hint of the disorder. The bands at around 150 and 175 cm$^{-1}$ are attributed to the NH$_4^+$-O stretch. The existence of two distinct bands is likely due to the different orientations of the ammonium molecule bonded within the M-site of the feldspar framework at room temperature.

On cooling the ammonium micas, although the bands corresponding to the internal modes of ammonium ions in mid-near infrared regions (Mookherjee et al., 2002a,b) show distinct changes at around 140 K (tobelite) and 130 K (phlogopite), the bands assigned in the far-infrared region, due to ND$_4^+$-O (Fig.3 and Fig.4) stretching show only weak changes. One has to bear in mind that far-infrared bands are mostly a combination of the lattice vibration and M-O stretching, where M is the interlayer cation or molecule. The M-O bond lengths are slightly greater than 3Å, i.e., only slightly less than the $a$ lattice parameter of a mica (around 5Å). It is likely that the
orientational ordering of the ammonium ion (reported previously, Mookherjee et al., 2002a,b) causes no significant change in the remainder of the structure, as we see very little change of the far-infrared bands.

**Conclusion**

We conclude that the far infrared bands are due to the combination of the torsion modes of the interlayer region and ND₄-O stretching modes. Although, from the near infrared region, internal modes of the ammonium ion show considerable changes attributed to the ammonium ordering (Mookherjee et al., 2002a,b), the fact that the far infrared bands do not show significant change on cooling indicate that the rest of the mica structure is essentially unaffected by the orientational ordering of the ammonium ions.

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Figure 1. FIR spectra of ND$_4$-tobelite, ND$_4$-phlogopite and phengite 2M$_1$ collected at room temperature.

Figure 2. FIR spectra for ND$_4$-buddingtonite and a disordered alkali feldspar shown for comparison.
Figure 3. Thermal evolution of ND₄-phlogopite in the far-infrared region.

Figure 4. Thermal evolution of ND₄-tobelite in the far-infrared region.