Far-infrared spectra of ammonium layer and framework silicates

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Abstract

The low-temperature behaviour of the ammonium mica: synthetic ND₄-tobelite and ND₄-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,

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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), Iiishi *et al.* (1971), Wyncke *et al.* (1981), and Paluszkiewivz and Zabinski (1992).

Here we extend these earlier studies and report the far infrared spectra of synthetic deuterated ammonium muscovite (ND₄-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 $2M_I$ (Mookherjee *et al.*, 2001). Finally, far-infrared spectra have also been obtained for synthetic ND₄-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 ND₄-tobelite, ND₄-phlogopite and ND₄-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})O₁₀(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 discshaped 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 to700 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 constrast, 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 ND₄⁺-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 ND₄-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 NH₄⁺-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

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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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References

Angino, E.E. (1968): Relation between chemical composition and far infrared spectra of plagioclase feldspars. Special Paper, Geological Society of America. p. 7. Geological Society of America (GSA). Boulder, CO, United States.

Angino, E.E. (1969): Far infrared absorption spectra of plagioclase feldspars. Short papers on research in 1968. Part 1, p. 9-11. Kansas Geological Survey, Lawrence, KS, United States.

Badreddine, R., Dred, R-L., and Prost, R. (2002a): A far infrared study of K⁺ ions during K⁺ \leftrightarrow Ca²⁺ exchange in vermiculite. *Clay Minerals*, **37**, 59-70.

Badreddine, R., Dred, R-L., and Prost, R. (2002b): Far infrared study of K^+ , Rb^+ and Cs^+ during their exchange with Na⁺ and Ca²⁺ in vermiculite. *Clay Minerals*, **37**, 71-81.

Boukili, B., Robert, J.L., Beny, J.M., and Holtz, F. (2001): Structural effects of OH→F substitution in trioctahedral micas of the system K₂O-FeO-Fe₂O₃-Al₂O₃-SiO₂ H₂O HF. *Schweizerische Mineralogische und Petrographische Mitteilungen*, **81**, 55-67.

Clegg, P.E., Pandya, S.J., Foster, S.A., and Bastin, J.A. (1972): Far infrared properties of lunar rock. *Proceedings of the 3rd Lunar Science Conference*, p. 3035-45. Pergamon, Oxford, UK.

Courtin, R., Lena, P., De, M.M., Rouan, D., Nicollier, C., and Wijnbergen, J. (1979): Far-infrared photometry of planets; Saturn and Venus. *Icarus*, **38**, 411-9

Diaz, M., Farmer, V.C., and Prost, R. (2000): Characterization and assignment of far infrared absorption bands of K^+ in muscovite. *Clays and Clay Minerals*, **48**, 433-8.

Diaz M., Huard, E. and Prost R. (2002a): Far infrared analysis of the structural environment of interlayer K^+ , NH_4^+ , Rb^+ and Cs^+ selectively retained by vermiculite. *Clays and Clay Minerals*, **50**, 284-293.

Diaz, M., Lapreche, V., Harsh, J., and Prost, R. (2002b): Far infrared spectra of K⁺ in dioctahedral and trioctahedral mixed-layer minerals. *American Mineralogist*, **87**, 1207-1214.

Gawarecki, S.J., Neal, J.T., Cronin, J., and Williams, R.S., Jr. (1969): Geologic information from satellite infrared imagery. In: *Satellite Imagery of the Earth*, 661-4. American Society of Photogrammetry, Falls Church, VA, United States.

Harlov, D.E., Andrut, M. and Poter, B. (2001a): Characterization of tobelite (NH4)(Al2)[AlSi3O10](OH) 2 and ND4- tobelite (ND4)(Al2)[AlSi3O10](OD) 2 using IR spectroscopy and Rietveld refinement of XRD spectra. *Physics and Chemistry of Minerals*, **28**, 268-276.

Harlov, D.E., Andrut, M. & Poter, B. (2001b): Characterization of NH₄- phlogopite (NH₄)(Mg₃)[AlSi₃O₁₀](OH)₂ and ND₄- phlogopite (ND₄)(Mg₃)[AlSi₃O₁₀](OD)₂ using

IR spectroscopy and Rietveld refinement of XRD spectra. *Physics and Chemistry of Minerals*, **28**, 77-866.

Harlov, D.E., Andrut, M. & Poter, B. (2001c): Characterization of buddingtonite (NH₄)[AlSi₃O₈] and ND₄- buddingtonite (ND₄)[AlSi₃O₈] using IR spectroscopy and Rietveld refinement of XRD spectra. *Physics and Chemistry of Minerals*, **28**(3), 188-198.

Harsh, J.B., Prost, R., Laperche, V., and Srodon, J. (1992): Far infrared spectroscopy of illite-smectites and illitic materials. In: *American Society of Agronomy, 84th Annual Meeting*. p. 372. American Society of Agronomy, Madison, WI, United States.

Ishii, M., Nakahira, M., and Takeda, H. (1969): Far infrared absorption spectra of micas. *International Clay Conference; Proceedings*, 1., 247-259. Israel Univ. Press Jerusalem, Israel.

Iiishi, K., Tomisaka, T., Kato, T., and Umegaki, Y. (1971): Isomorphous substitution and infrared and far infrared spectra of the feldspar group. *Neues Jahrbuch fuer Mineralogie Abhandlungen*, **115**, 98-119

Laperche, V., and Prost, R. (1991): Assignment of the far-infrared absorption bands of K in micas. *Clays and Clay Minerals*, **39**, 281-289.

Liu, Y. (1996): Far-infrared spectroscopy of interlayer release of K from illite. *Acta Mineralogica Sinica*, **16**, 340-8.

Mookherjee M, Redfern S A T, and Zhang M (2001): Thermal response of structure and hydroxyl ion of phengite $2M_1$: an in situ neutron diffraction and FTIR study. *European Journal of Mineralogy*, **13**, 545-555.

Mookherjee M., and Redfern, S.A.T. (2002): A high-temperature Fourier transform infrared studyof the interlayer and Si-O stretching region in phengite- $2M_1$. *Clay Minerals*, **37**, 309-321.

Mookherjee, M., Redfern, S.A.T., Zhang, M., Harlov, D.E.(2002a): Orientational order-disorder of $N(D,H)_4^+$ in tobelite. *American Mineralogist.* **87**,1868-1891.

Mookherjee, M., Redfern, S.A.T., Zhang, M., Harlov, D.E. (2002b): Orientational order-disorder of ND_4^+/NH_4^+ in synthetic ND_4/NH_4 -phlogopite: a low-temperature infrared study. *European Journal of Mineralogy*, **14**, 1033-1039.

Paluszkiewivz, C., and Zabinski, W. (1992): Far infrared spectra of vesuvianite; preliminary report. *Mineralogia Polonica*, **23**, 13-6.

Perry, C.H., Agrawal, D.K., Anastassakis, E., Lowndes, R.P., and Tornberg, N.E.
(1972): Far infrared and Raman spectroscopic investigations of lunar materials from
Apollo 11, 12, 14, and 15. *Proceedings of the 3rd Lunar Science Conference*, p. 3077
95. Pergamon, Oxford, International

Prost, R., and Laperche, V. (1988): Far infrared study of potassium in micas. In: *Clay Minerals Society, 25th Annual Meeting; Abstracts*, p. 89. Clay Minerals Society, United States.

Prost, R., and Laperche, V. (1990): Far-infrared study of potassium in micas. *Clays* and *Clay Minerals*, **38**, 351-5.

Pugh, M.J., and Bastin, J.A. (1975): Far-infrared observation of lunar rock. In C.
Karr, Jr., Ed. *Infrared and Raman spectroscopy of lunar and terrestrial minerals*. p.
255-72. Academic Press, New York, N.Y., United States.

Schroeder, P.A. (1988): Far infra-red spectroscopy of potassium interlayered phyllosilicates. In: *Clay Minerals Society, 25th Annual Meeting; Abstracts*, p. 88. Clay Minerals Society, United States.

Schroeder, P.A. (1991): Far infrared spectroscopy of mixed-layer illite/ smectites. In: *Clay Minerals Society, 28th Annual Meeting, Program and Abstracts*, p. 137. Clay Minerals Society, United States.

Schroeder, P.A. (1992): Far-infrared study of the interlayer torsional-vibrational mode of mixed-layer illite/smectites. *Clays and Clay Minerals*, **40**, 81-91.

Tateyama, H., Shimoda, S., and Sudo, T. (1977): Estimation of K-O distance and tetrahedral rotation angle of K-micas from far-infrared absorption spectra data. *American Mineralogist*, **62**, 534-9.

Velde, B., and Couty, R. (1985): Far infrared spectra of hydrous layer silicates. *Physics and Chemistry of Minerals*, **12**, 347-52.

Vickers, D.G., and Bastin, J.A. (1977): The interaction of lunar rock and far infrared radiation. *Philosophical Transactions of the Royal Society of London, Series A: Mathematical and Physical Sciences*, 285, 319-24.

Ward, D.B., Gull, G.E., and Harwit, M. (1977): Far-infrared spectral observations of Venus, Mars, and Jupiter. *Icarus*, **30**, 295-300.

Wyncke, B., McMillan, P.F., Brown, W.L., Openshaw, R.E., and Brehat, F. (1981): A room-temperature phase transition in maximum microcline; absorption in the far infrared (10-200 cm⁻¹) in the temperature range 110-300 K. *Physics and Chemistry of Minerals*, **7**, 31-4.



Figure 1. FIR spectra of ND₄-tobelite, ND₄-phlogopite and phengite $2M_1$ collected at room temperature.



Figure 2. FIR spectra for ND₄-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.