Vibrational Spectroscopic Studies of Layered Silicates

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The FT-IR and FT-Raman spectra of three-layered silicates, magadiite, kenyaite, and ilerite have been measured. The correlation between vibrational spectra and the structural properties of silicates under investigation has been made. The unit cells of all three silicates appear to be centrosymmetric since the mutual exclusion rule applies. The factor group symmetries of magadiite and ilerite may be C_{2h}. The unit cell symmetry of kenyaite is either C_{4h} or D_{4h}. All three silicates have multilayer structures with five- and six-membered rings. For magadiite and kenyaite, some Si−O−Si linkages with very large bond angles near 180° may exist. Hydrogen bonding occurs in all three silicates, but not all of the hydroxyl groups are involved. The structure of ilerite may not be related to those of magadiite and kenyaite as closely as previously thought since its vibrational spectra are distinctly different from those of magadiite and kenyaite in many aspects.

Introduction

Magadiite, ilerite, and kenyaite are related hydrous alkali silicates with multilayered structures.[1,2] The minerals magadiite and kenyaite were first found in the deposits of Lake Magadi, Kenya and described by Eugster in 1967.[3] The chemical compositions of the natural samples were reported as $Na_2Si_{14}O_{29}\cdot 9H_2O$ (magadiite) and $Na_2Si_{20}O_{41}\cdot 10H_2O$ (kenyaite). These two silicates can be readily prepared in the laboratory by hydrothermal synthesis. Ilerite, commonly known as octosilicate, does not have a corresponding mineral form in nature. The term “ilerite” was named after R. K. Iler who first synthesized and studied this silicate in 1964.[4] The name “octosilicate” was obtained on the basis of its chemical composition ($Na_2Si_8O_{17}\cdot 9H_2O$) in which the SiO_2/Na_2O ratio is equal to 8.[5]

These hydrated layered alkali-metal silicates exhibit some interesting properties such as interlamellar sorption of water and organic molecules and ion exchange of the surface cations. These properties suggest potential practical applications as ion exchangers, adsorbents, catalysts, and molecular sieves. Recently, these layered silicates have received much attention because of their ability to transform to layered silicic acids by proton exchange. Layered silicic acids are very useful hosts in the formation of pillared materials because of the presence of reactive silanol groups in their interlayer surfaces.

The structures of these silicates have been of continuous interest in past decades because the physical and chemical properties of these materials are largely structure-dependent. However, the exact structures of magadiite, ilerite, and kenyaite are unknown because it is difficult to grow a single crystal suitable for single-crystal X-ray diffraction analysis. Consequently, most of the structural information has been obtained by using techniques such as solid-state NMR[1,2,6−12] and powder X-ray diffraction.[3,5,6,13] Several models have been proposed for the structures of these materials, most of which are based on the results of ^{29}Si NMR studies.[1,2,6−9]

Vibrational spectroscopy can also provide valuable structural information which is complementary to that obtained from XRD and NMR. In the past, the vibrational approach has been utilized to obtain the structural properties of crystalline silicates[14] and silicate glasses and melts.[15−16] Recently, we have examined the vibrational spectra of singly-layered silicates, kanemite,[17] silinaite, and makatite[18] which are structurally

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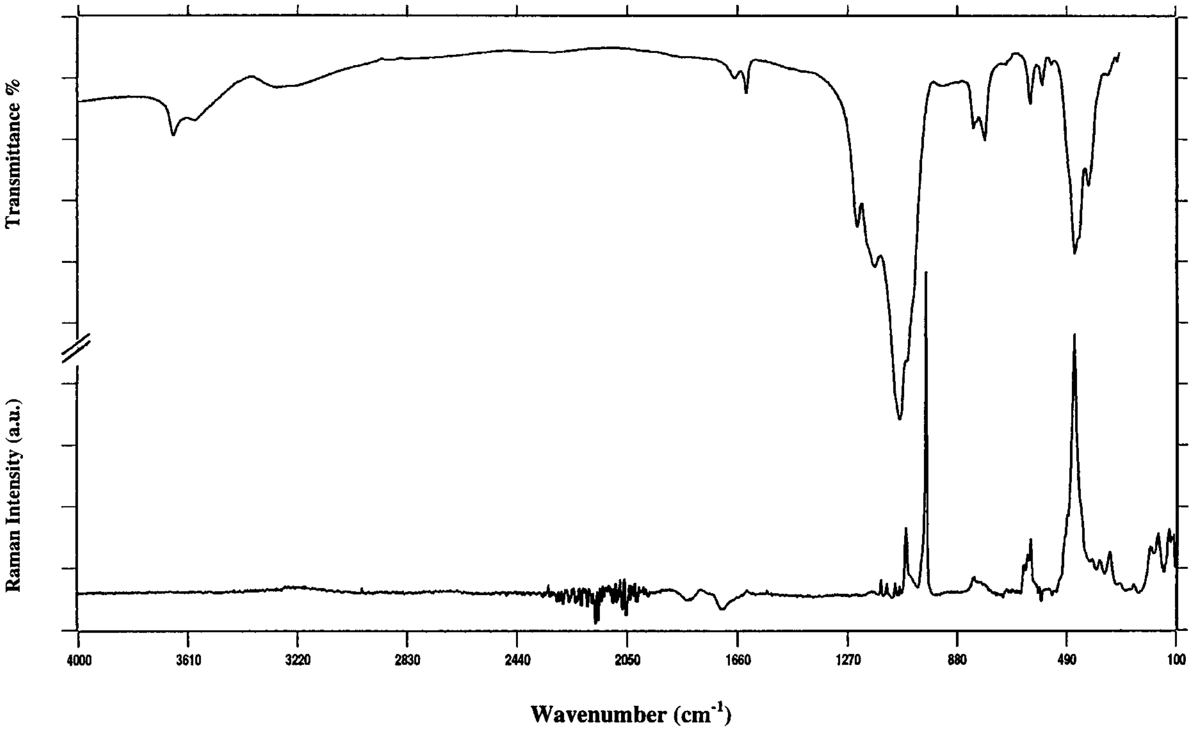

Figure 1. IR (top) and Raman (bottom) spectra of magadiite. (The anomalous signals in the region 2600−1500 cm^{-1} (of Raman spectrum) are due to the instrument response and the artifacts introduced by base line correction.)

related to magadiite, ilerite, and kenyaite.[1,2] For silinaite and makatite, whose structures have been determined by single-crystal X-ray diffraction, vibrational features of these materials have been correlated to their crystal structure. For kanemite with unknown structure, its vibrational spectra have been interpreted by using the results derived from silinaite, makatite, and other related silicates with known structures. Using IR and Raman data, we were able not only to obtain invaluable information regarding the hydrogen bonding, Si−O−Si bond angles, the network connectivity, and the size of the ring systems formed by SiO_4 tetrahedra in kanemite but also to differentiate unambiguously the two space groups proposed by previous powder XRD studies.[17] In the present work, we have extended our infrared and Raman spectroscopic studies to include magadiite, ilerite, and kenyaite with particular attention being paid to the correlation of the vibrational properties of these materials with their structural features. Although IR spectra were previously used to study the interlayer surface and the structure, the data in the literature are incomplete. To date, no Raman studies have been performed on these silicates. The combination of both infrared and Raman is particularly appropriate since the two techniques have different selection rules.

Experimental Section

Magadiite, ilerite, and kenyaite were synthesized according to refs 5, 19, and 20, respectively. The purity and crystallinity were checked by powder X-ray diffraction measurements (Philips PW 1830 powder diffractometer). The IR spectra were recorded on a Perkin-Elmer Paragon-1000 FT-IR spectrometer equipped with a DTGS detector. Samples were prepared using the standard KBr method. We were unable to obtain IR spectra below 300 cm^{-1} because of the limitation of the instrument. The Raman spectra were obtained on a Bruker RFS-100 FT-Raman spectrometer equipped with a Nd^{3+}:YAG laser (1064.1 nm) and a liquid nitrogen cooled Ge detector. The laser power at the sample was approximately 90 mW and 6000 scans were accumulated for the spectra. Base line correction was performed on all the Raman spectra. All the measurements were performed at room temperature. The spectral resolution was 2 cm^{-1} for both IR and Raman measurements.

Results and Discussion

The vibrational spectra of magadiite, kenyaite, and ilerite are shown in Figures 1−3 and their corresponding IR and Raman frequencies are given in Tables 1−3, respectively. By inspection of the tables, it becomes immediately evident that for all three silicates all of the observed IR bands appear at different frequencies than those in the Raman spectra, with the exception of the band at 620 cm^{-1} in the magadiite spectra, which is probably due to accidental degeneracy. The fact that IR and Raman bands were noncoincident implies that the unit cells of three silicates are centrosymmetric since the principle of mutual exclusion applies. Previous powder X-ray diffraction studies suggested that magadiite[3] and ilerite[5] belong to the monoclinic crystal system, whereas the structure of kenyaite is tetragonal.[3] Since the space groups of these silicates must have a center of symmetry, the possible space groups for magadiite and ilerite can now be limited to those in the $2/m$ (C_{2h}) class of the monoclinic system. For kenyaite the unit cell symmetry is either $4/m$ (C_{4h}) or $4/mmm$ (D_{4h}) of the tetragonal system.

The vibrational spectra of these silicates can be divided into two regions. The first region covers the frequency range 4000−1600 cm^{-1} where stretching and bending vibrations of water molecules appear. The

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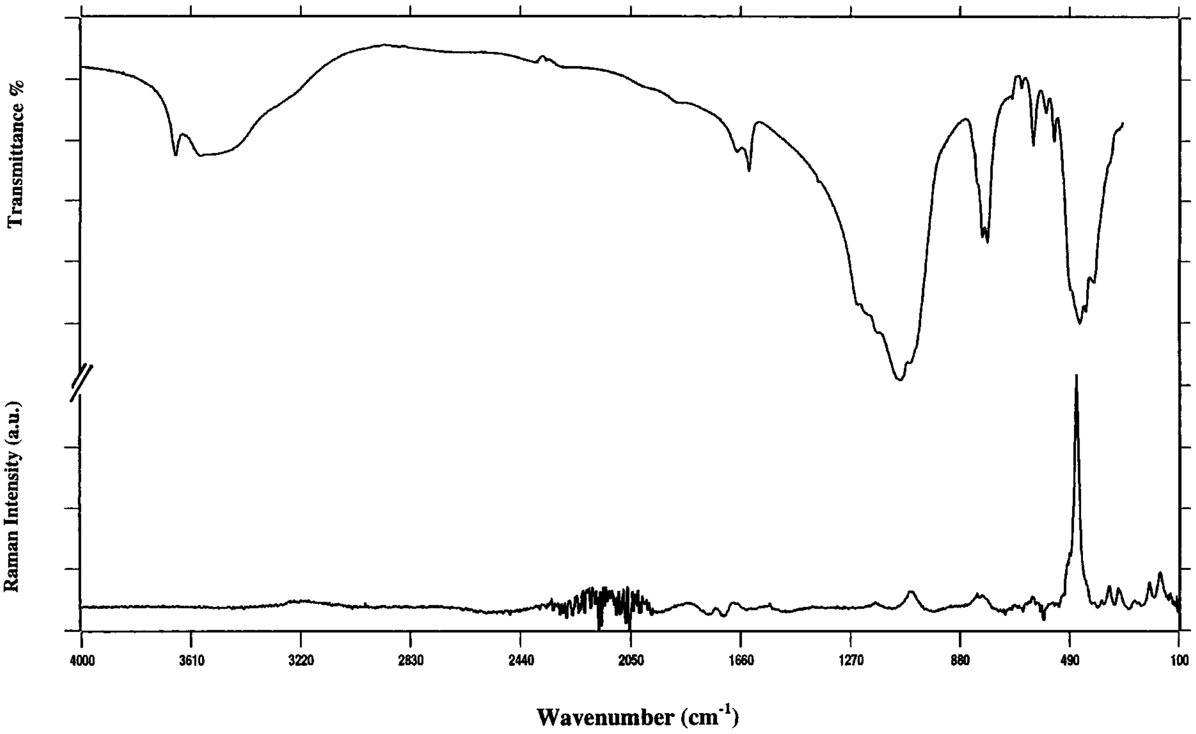

Figure 2. IR (top) and Raman (bottom) spectra of kenyaite. (The anomalous signals in the region 2600–1500 cm^{-1} (of Raman spectrum) are due to the instrument response and the artifacts introduced by base line correction.)

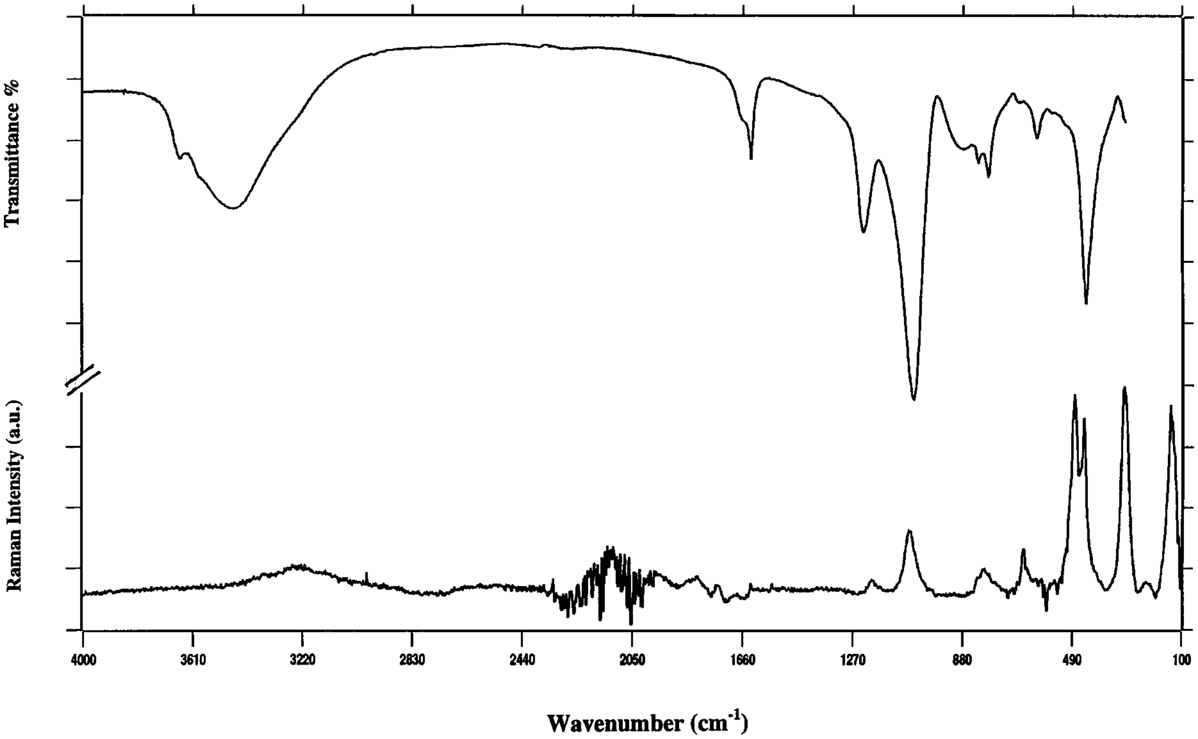

Figure 3. IR (top) and Raman (bottom) spectra of ilerite. (The anomalous signals in the region 2600–1500 cm^{-1} (of Raman Spectrum) are due to the instrument response and the artifacts introduced by base line correction.)

second region (below 1300 cm^{-1}) includes the vibrations due to the silicate layer and charge-balancing cations. Since the vibrations in these two regions are not usually coupled to each other, we shall discuss them separately.

Vibrations of Silicate Layer and Associated Cations. The tentative assignments for the spectra of three silicates are given in Tables 1–3. It is widely accepted that the vibrations due to the silicate layer and associated cations follow the frequency order[14,15] ν_{as}(Si–O–Si) > ν(Si–O$^-$) > ν_s(Si–O–Si) > δ(Si–O–Si), δ(O–Si–O), and ν(Na-O) where ν_{as}(Si–O–Si) and ν_s(Si–O–Si) refer to the asymmetric and symmetric stretching modes of Si–O–Si bridges; ν(Si–O$^-$) represents the stretching modes of terminal Si–O$^-$ bonds from Q^3 units; δ(Si–O–Si) and δ(O–Si–O) refer to the Si–O–Si and O–Si–O bending modes; ν(Na–O) represents the Na–O stretching modes. Generally, it is rather difficult to calculate the normal modes and

Table 1. Vibrational Data (cm^{-1}) for Magadiite and Their Assignments

IR	Raman		assignment
3660 m			ν(OH)
3585 m			
3293 w,br			
	3266 vw, br		
3230 w,br			
1668 m			δ(HOH)
1628 m			
1235 m		five-membered ring	ν_{as}(Si−O−Si)
1200 (sh)			
	1184 vw		
1174 s		∠Si−O−Si =180°	
	1151 w		
	1131 w		
	1101 w		
1087 vs			ν(Si−O$^-$)
	1085 w		
	1064 m		
1061 (sh)			
	1049 vw		
	992 vs		
939 vw			
	823 w		ν_s'(Si−O−Si)
822 m			
	792 vw		
783 m			
709 vw			
	705 vw		
693 vw			ν_s(Si−O−Si)
	674 vw		
	645 w		
	632 w		
620 m			
	620 m		
	587 vw		
577 m			
545 w			
	488 (sh)		
	464 vs	six-membered ring	
461 vs			
443 (sh)			
	442 (sh)		
413 s			
	398 w		δSi−O−Si); δ(O−Si−O); ν(Na-O); and external modes of H_2O
	373 w		
353 vw			
346 vw			
339 vw			
	336 w		
334 vw			
323 w			
310 w			
	299 vw		
	252 vw		
	192 w		
	163 m		
	124 m		
	113 w		
	107 m		

frequencies of framework and layered silicates as a result of problems such as how to describe the vibrational motions of an infinite framework with a finite model (various SiO_4 rings and other building units) and how to obtain a reasonable force constant set suitable for the silicate framework or layer. Consequently, some simplified models have been widely utilized. For example, the possible types of normal modes in silicates derived from SiO_4 tetrahedra have been reviewed by McMillan[15] and are briefly described as follows: the stretching vibrations of a free tetrahedral SiO_4 unit can be described by the nondegenerate total symmetric (ν_1) and the triply degenerate asymmetric stretching (ν_3) modes (Figure 4A). For the framework silicates and silicates with multilayer structures, including those under investigation, their formation may be considered as polymerization of SiO_4 tetrahedra by corner-sharing each oxygen with two SiO_4 units. This results in a coupling of ν_1 and ν_3 types of modes.[15] According to the model proposed by Sen and Thorpe[21] for condensed SiO_2 systems where silicon is tetrahedrally coordinated by oxygen and the oxygen 2-fold coordinated by silicon, the vibrational coupling results in two sets of stretching vibrations, both of which can be described by the stretching motions of adjacent Si−O bonds linked at the oxygen. The high-frequency set of modes, ν_{as}(Si−O−Si),

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(21) Sen, P. N.; Thorpe, M. F. *Phys. Rev. B* **1977**, *15*, 4030.

Table 2. Vibrational Data (cm^{-1}) for Kenyaite and Their Assignments

IR	Raman		assignment
3664 m			ν(OH)
3571 m			
3458 m,br			
	3200 vw,br		
1672 m			δ(HOH)
1629 m			
1242 s		five-membered ring	ν_{as}(Si−O−Si)
1204 (sh)			
	1179 w		
1169 s		∠Si−O−Si=180°	
1091 vs			ν(Si−O$^-$)
	1061 w		
1057 s			
	1049 w		
	819 w		ν_s'(Si−O−Si)
	801 vw		
799 s			
782 s			
	780 vw		
696 vw			ν_s(Si−O−Si)
661 w			
	622 w		
619 m			
574 w			
545 m			
	493 (sh)		
488 (sh)			
	465 vs	six-membered ring	
453 vs			
	431 (sh)		
430 s			
401 s			
	398 vw		δ(Si−O−Si); δ(O−Si−O); ν(Na-O); external modes of H_2O
	376 w		
	349 w		
346 (sh)			
	316 w		
	258 w		
	242 vw		
	204 w		
	166 w		
	162 w		
	155 vw		
	148 vw		
	139 vw		
	129 vw		
	123 vw		
	115 vw		
	106 w		

results from the out-of-phase coupling between two adjacent Si−O stretches, giving a resultant oxygen motion subparallel to the Si−Si line, and a low-frequency set of modes, ν_s(Si−O−Si), resulting from the in-phase coupling with the resultant oxygen motion in the plane bisecting the Si−O−Si bond (Figure 4B).[15] In general, the ν_{as}(Si−O−Si) modes appear in the region 1200−1000 cm^{-1}, whereas ν_s(Si−O−Si) appears in the region 700−400 cm^{-1}. The vibrational modes near 800 cm^{-1} involve predominately silicon motion (Figure 4C)[22] labeled as ν_s'(Si−O−Si). Magadiite, ilerite, and kenyaite all contain Q^3 species and the corresponding ν(Si−O$^-$) stretching vibrations are normally observed in the region 1100−1050 cm^{-1}.[14−16]

On the basis of the above discussion, for all three silicates under investigation we tentatively assign the bands between 1300 and 950 cm^{-1} to the asymmetric stretching vibrations of Si−O−Si linkages, ν_{as}(Si−O−Si), and the stretching vibrations of terminal Si−O$^-$ bonds, ν(Si−O$^-$). The bands between 700 and 400 cm^{-1} are associated with the symmetric stretching vibrations of Si−O−Si bridges, ν_s(Si−O−Si). The bands near 800 cm^{-1} are due to the ν_s'(Si−O−Si). The bands below 400 cm^{-1} are due to the silicon−oxygen bending and torsional vibrations, δ(Si−O−Si) and δ(O−Si−O), and the stretching vibrations arising from Na−O.

Magadiite, kenyaite, and ilerite exhibit IR bands, at 1235, 1242, and 1231 cm^{-1}, respectively (Tables 1−3). As mentioned above, these high-frequency bands can be assigned to the asymmetric stretching of Si−O−Si bridges, ν_{as}(Si−O−Si). In mordenite and pentasil zeolites such as ZSM-5 and ZSM-11, Jansen et al.[23] found that the IR bands at about 1225 cm^{-1} are characteristic of the five-membered rings in these zeolites. By analogy, Garcés and co-workers interpreted their observed IR band of magadiite at 1237 cm^{-1} as the indication of an

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(22) Laughlin, R. B.; Joannopoulos, J. D. *Phys. Rev. B* **1977**, *16*, 2942.

(23) Jansen, J. C.; van der Gaag, F. J.; van Bekkum, H. *Zeolites* **1984**, *4*, 369.

Table 3. Vibrational Data (cm^{-1}) for Ilerite and Their Assignments

IR	Raman	assignment	
3654 s			ν(OH)
3589 s			
3462 s,br			
	3250 vw,br		
1663 m (sh)			δ(HOH)
1630 s			
1231 s		five-membered ring	ν_{as}(Si−O−Si)
	1202 w		
	1071 m		ν(Si−O$^-$)
1055 vs			
878 m			ν_s'(Si−O−Si)
	830 w		
825 m			
	802 w		
789 s			
	778 vw		
680 vw			ν_s(Si−O−Si)
	663 m		
617 m			
515 vw			
	483 s	six-membered ring	
	449 s	six-membered ring	
441 vs			
	305 s		δ(Si−O−Si); δ(O−Si−O); ν(Na−O); external modes of H_2O
	226 w		
	139 s		
	133 (sh)		
	123 (sh)		
	107 w		

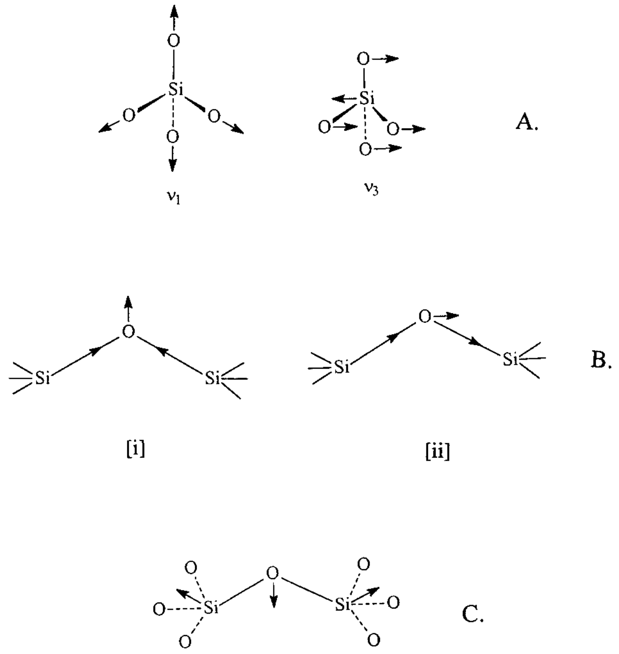

Figure 4. Schematic representations of simplified normal modes in silicates. (A) Stretching vibrations of a free SiO_4 unit. (B) [i] The in-phase (low-frequency), ν_s(Si−O−Si), and [ii] out-of-phase (high-frequency), ν_{as}(Si−O−Si), vibrations of two coupled Si−O stretching motions. (C) Silicon "cage" motion, ν_s'(Si−O−Si), near 800 cm^{-1}. Drawing after ref 15.

existing five-membered ring in the structure.[7] Although this assignment is very much at the empirical level, it has been widely accepted by the zeolite community because this mode has been observed in the IR spectra of many zeolites containing five-membered rings with known structures, including silicalite, ZSM-5, ZSM-11, modernite, boralite, ferrierite, epistilbite, dachiardite, ZSM-12, ZSM-22, and ZSM-23 (and so forth).[24] This assignment has been used to identify the structural units in zeolites with unknown structure such as ZSM-35.[24] Thus, in the present study, we support the interpretation of Garcés et al.[7] and assign the high-frequency bands in the respective IR spectra of magadiite, kenyaite, and ilerite to the ν_{as}(Si−O−Si) mode characteristic of five-membered rings in their structures.

Magadiite exhibits another high-frequency IR band at 1174 cm^{-1} with a shoulder at 1200 cm^{-1}. A similar band at 1169 cm^{-1} with a shoulder at 1204 cm^{-1} is found in the IR spectrum of kenyaite. By studying the IR spectrum of pyrosilicates containing the Si_2O_7 group, where $\angle$SiOSi = 180°, Lazarev has suggested that the appearance of IR bands in the frequency range between 1150 and 1200 cm^{-1} is associated with the existence of Si−O−Si bridges with an angle of 180° (or nearly so).[14] Later, this assumption was extended to include other silicates with more complicated structures than pyrosilicates and confirmed by X-ray diffraction.[14] In our recent study of silinaite (a singly-layered silicate), we observed two narrow intense IR bands at 1189 and 1159 cm^{-1}, which is also interpreted as an indication of existing linear Si−O−Si linkages.[18] In this case, the interpretation was supported by single-crystal X-ray diffraction data[25] showing that silinaite indeed contains the Si−O−Si linkages with 180° bond angles. Thus, we suggest that both magadiite and kenyaite contain certain Si−O−Si bonds with very large angles, close to 180°. The identification of linear Si−O−Si linkages in magadiite and kenyaite provides additional evidence that there are five-membered rings in the structures of these materials because assuming O−Si−O angles in a planar five-membered SiO_4 ring are 109.5°, the Si−O−Si angles should be 178.5°.[26]

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(24) Szostak, R. *Molecular Sieves: Principles of Synthesis and Identification*; Van Nostrand Reihold: New York, 1989; pp 323−326.
(25) Grice, J. D. *Can. Miner.* **1991**, *29*, 363.
(26) Galeener, F. L. *J. Non-Cryst. Solids* **1982**, *49*, 53.

In contrast to the singly-layered silicates such as makatite[18] and kanemite,[17] magadiite, kenyaite, and ilerite do not have very strong Raman bands in the range 1100−1050 cm^{-1}. The bands (1064, 1061, and 1071 cm^{-1} for magadiite, kenyaite, and ilerite, respectively) observed in this region only have medium or weak intensities. Weak bands also appear in the higher frequency region, above 1100 cm^{-1}. These observations indicate that the structures of magadiite, kenyaite, and ilerite contain not only Q^3 but also Q^4 species. This result suggests that these materials do have multilayer structures, which is consistent with a previous high-resolution solid-state ^{29}Si NMR study.[6,8] Magadiite has a strong band at 992 cm^{-1} in its Raman spectrum. The strong Raman bands in the 1100−1050 cm^{-1} region are usually associated with the stretching vibrations of the terminal nonbridging oxygens, $\nu(\mathrm{Si{-}O^-})$, in the Q^3 species.[15,27−29] Although the strong Raman band of magadiite at 992 cm^{-1} is not exactly located in this region, we can still reasonably assume that this band is due to the $\nu(\mathrm{Si{-}O^-})$ of Q^3 species since the previous solid-state ^{29}Si NMR study has revealed the presence of a large number of Q^3 units in the structure of magadiite (Q^3:Q^4 = 1:2 ref 6 and 1:3 ref 8). The appearance of the $\nu(\mathrm{Si{-}O^-})$ band at a lower frequency for magadiite may suggest that the interactions between the Si−O$^-$ in some of the Q^3 units and the sodium ions are quite strong because strong cation−oxygen interactions weaken the Si−O$^-$ bond, resulting in a lower Si−O$^-$ stretching frequency.

Strong bands are observed at 464 and 465 cm^{-1} in the Raman spectra of magadiite and kenyaite, respectively. As mentioned earlier, the Raman bands in the region 700−400 cm^{-1} are due to ν_s(Si−O−Si) modes. Since vibrations in this region are very sensitive to the Si−O−Si bond angles and network connectivity, much effort has been made theoretically[26,30] and experimentally[28,31−34] toward establishing the relationship between the frequency of the strongest ν_s(Si−O−Si) band and the structural properties such as the average T−O−T angle (T = Si and Al) and the ring configurations in silicates and aluminosilicates. For example, Dutta and co-workers have found empirically that the frequency of the strongest ν_s(T−O−T) band has an inverse dependence on the magnitude of the average T−O−T angles in various framework aluminosilicates (zeolites).[34] Sharma and co-workers have demonstrated that the frequency of the strongest ν_s(Si−O−Si) band can be related to the dominant size of SiO_4 rings in the structure of the silicates.[28,31−33] In particular, observation of distinct Raman bands in the frequency region 480−400 cm^{-1} are characteristic of six-membered rings of silicon−oxygen tetrahedra. Following the above assignment, we tentatively suggest that the appearance of strong Raman bands at 464 and 465 cm^{-1} for magadiite and kenyaite infer that the structures of these materials may consist predominantly of six-membered rings of silicon−oxygen tetrahedra. This assignment is consistent with several proposed structural models in the literature which also contain predominantly six-membered rings.[7−9]

Two strong bands at 449 and 483 cm^{-1} appear in the Raman spectrum of ilerite. These bands are also interpreted as the symmetric stretching vibrational modes of Si−O−Si linkages characteristic of six-membered rings of silicon−oxygen tetrahedra. The two well-separated, strong bands with approximately equal intensities in the Raman spectrum of ilerite may be due to the existence of two distinct types of six-membered rings, with the lower frequency (449 cm^{-1}) band corresponding to the six-membered rings with a slightly larger average Si−O−Si angle. It was previously suggested that the structure of ilerite is closely related to those of magadiite and kenyaite.[1−2,6] However, since many distinct differences between the spectra of ilerite and those of magadiite and kenyaite were observed, the structure of ilerite seems to be quite different from those of magadiite and kenyaite.

It is difficult to make the detailed assignments of the vibrational bands below 400 cm^{-1}. These vibrations are mainly due to the bending vibrations, δ(Si−O−Si), δ(O−Si−O), and $\delta(\mathrm{Si{-}O^-})$; the rotational and translational modes of water molecules; the translational motion of sodium.

Internal Vibrations of Water Molecules. In general, the stretching vibrations of the OH groups (νOH) of water molecules in hydrated silicates are observed in the region 3700−3000 cm^{-1}.[14] In this region, the IR spectrum of magadiite shows two sets of OH stretching bands: two relatively sharp peaks at higher frequencies (3660 and 3585 cm^{-1}) and two very broad, overlapping bands at lower frequencies (3293 and 3230 cm^{-1}). The broad low-frequency bands are related to the OH groups involved in interlayer hydrogen bonding. The presence of strong hydrogen bonding in magadiite is also suggested by Almond et al. based on the results from $^1\mathrm{H} \rightarrow {}^{29}\mathrm{Si}$ cross polarization experiments.[12] The narrow bands at higher frequency can be assigned to the isolated OH groups, suggesting that not all of the water hydroxyl groups are involved in strong hydrogen bonding. Similarly, kenyaite and ilerite show two types of OH stretching bands: a broad band at lower frequency near 3460 cm^{-1} due to strong hydrogen bonding and sharp bands (one for kenyaite and two for ilerite) in a higher frequency region 3560−3670 cm^{-1} corresponding to free hydroxyl groups. For all three silicates the bending modes of water molecules were observed as a doublet in the region 1670−1620 cm^{-1}. Observation of two bending modes may be attributed to either the existence of several crystallographically nonequivalent water molecules in the unit cell or the correlation splitting of ν_2 (A_1 related species).

The structural information obtained from our Raman and IR data indicate that magadiite and kenyaite both contain six- and five-membered rings and near linear Si−O−Si linkages. The structure of kenyaite appears to be similar to that of magadiite due to the similarity of the IR and Raman spectra (with the exception of the

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Raman band at 992 cm^{-1} observed for magadiite). This seems to be consistent with Eugster's suggestion that kenyaite is an alteration product of magadiite.[3] Since magadiite and kenyaite have different basal spacings,[1] it may be suggested that the sheets of kenyaite and magadiite are built up from different numbers of identical monolayers.

The spectra of kanemite[17] also bear some resemblance to those of magadiite and kenyaite. For example, a high-frequency band at about 1170 cm^{-1} assigned to the asymmetric stretching vibrations of Si−O−Si bridges with angles close to 180° ν_{as}(Si−O−Si) is also observed in the kanemite IR spectrum. In its Raman spectrum, a strong band at 465 cm^{-1} is observed, which is assigned to the symmetric vibrations of Si−O−Si linkages characteristic of six-membered rings in the structure. These common features found for kanemite, magadiite, and kenyaite indicate that a structural relationship may exist between these silicates. The multilayers in magadiite and kenyaite are probably built up from a varying number of single layers similar to that of kanemite. This argument is consistent with the fact that magadiite can be easily converted to kanemite, suggesting that it may be structurally related to kanemite. However, since no band was observed near 1230 cm^{-1} in its IR spectrum, kanemite does not seem to have five-membered rings in its structure. This may imply that the five-membered rings existing in magadiite and kenyaite are only in the blocks, which is consistent with the hypothetical structure of magadiite proposed by Garcés et al.[7]

Summary

Vibrational spectra of magadiite, kenyaite, and ilerite have been measured. The results suggest the following conclusions:

1. The unit cells of all three silicates appear to be centrosymmetric since the mutual exclusion rule applies. The factor group symmetries of magadiite and ilerite may be C_{2h}. The unit cell symmetry of kenyaite is either C_{4h} or D_{4h}.
2. All three silicates have multilayer structures with five- and six-membered rings.
3. For magadiite and kenyaite, some Si−O−Si linkages with very large bond angles near 180° may exist.
4. Hydrogen bonding occurs in all three silicates, but not all of the hydroxyl groups are involved.
5. The structure of ilerite may not be related to those of magadiite and kenyaite as closely as previously thought since its vibrational spectra are distinctly different from those of magadiite and kenyaite in many aspects.

It is hoped that the new information presented in this paper will stimulate more structural studies of these interesting materials.

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