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Infrared spectra of synthetic micas in the series muscovite–MgAl celadonite

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Abstract

Infrared spectra of synthetic potassic dioctahedral micas (muscovite–celadonite) indicate that ordering occurs in the two octahedral sites when more than 50 percent of the MgAl celadonite mica component is present. The appearance of doublets for certain vibrations suggests that there might be more than one type of Si–O network at intermediate compositions in the series. The Si–O apical vibration exhibits a single mode evolution. The vibrational energy–tetrahedral site occupancy relation for some other synthetic mica series shows that the energy of this band depends upon both the aluminum–silicon substitution and the structural type of mica involved. Octahedrally-coordinated ionic species do not seem to affect this vibrational energy. It seems that octahedral ions are not closely related to the apical oxygens in the Si–O network.

Introduction

The use of closely spaced members of a compositional mineral series in studies of infrared spectral properties is a valuable technique in studies of silicates. The present work is used to show some of the advantages of such a technique using synthetic micas.

Experimental

Infrared absorption spectra were recorded on a Digilab Fourier transform interferometer. 450-mg KBr discs having a 0.3 percent mineral concentration were used for the 1200–400 cm^{-1} range. Samples (about 1 mg) sedimented on polyethylene (handiwrap) sheets or self-supporting films were used in the 400–75 cm^{-1} range. Some of these preparations were used to determine the effect of preferred orientation of the mica flake on the spectra in the 1200–400 cm^{-1} range. It was found that one band (number 1, Fig. 2) was diminished almost entirely in intensity by this type of preparation and a second (number 14) was greatly diminished.

Muscovite–celadonite solid solution

Synthesis of micas in the system muscovite–celadonite has been accomplished previously (Wise and Eugster, 1964; Velde, 1965). From these studies, it appears that the only complete solid solution likely to be found in nature is that between muscovite [$KAl_2(Si_3Al)O_{10}OH_2$] and magnesian celadonite [$KMgAlSi_4O_{10}(OH)_2$]. This celadonite end member can be produced only at high pressure in the laboratory (> 10 kbar at 300°C). However, the synthetic micas do not decompose at atmospheric conditions for periods of 12–15 years.

The substitutional series takes place in two sites in the mica structure, the tetrahedrally-coordinated cation sites ($Si_3Al \rightleftarrows Si_4$) and the octahedrally-coordinated sites ($Al_2 \rightleftarrows MgAl$). The series is relatively simple. The polymorph of the micas synthesized is usually a mixture of 1M and 1Md types (Yoder and Eugster, 1955). A 1M and a 1M + 2M muscovite were also prepared. The series of micas studied here was synthesized at 8–10 kbar, 325°C, after 4–5 days under these conditions (see Velde, 1965, for details). Deuterated muscovite and 80 percent celadonite were also prepared. X-ray diffraction and the infrared spectra indicated pure single-phase synthesis products.

Figure 1 shows representative spectra in the mica series studied. Attributions of the vibration modes between 1200–75 cm^{-1} are based mainly on the descriptions given in Farmer (1974). Few new assignments are made. The various major absorption bands are numbered in consecutive order from high to low wave number. A graphical representation is given in Figure 2.

Some new observations were made. It appears that band 5, an Al–OH libration, becomes sharper for muscovite in the polymorphic sequence 1Md → 1M

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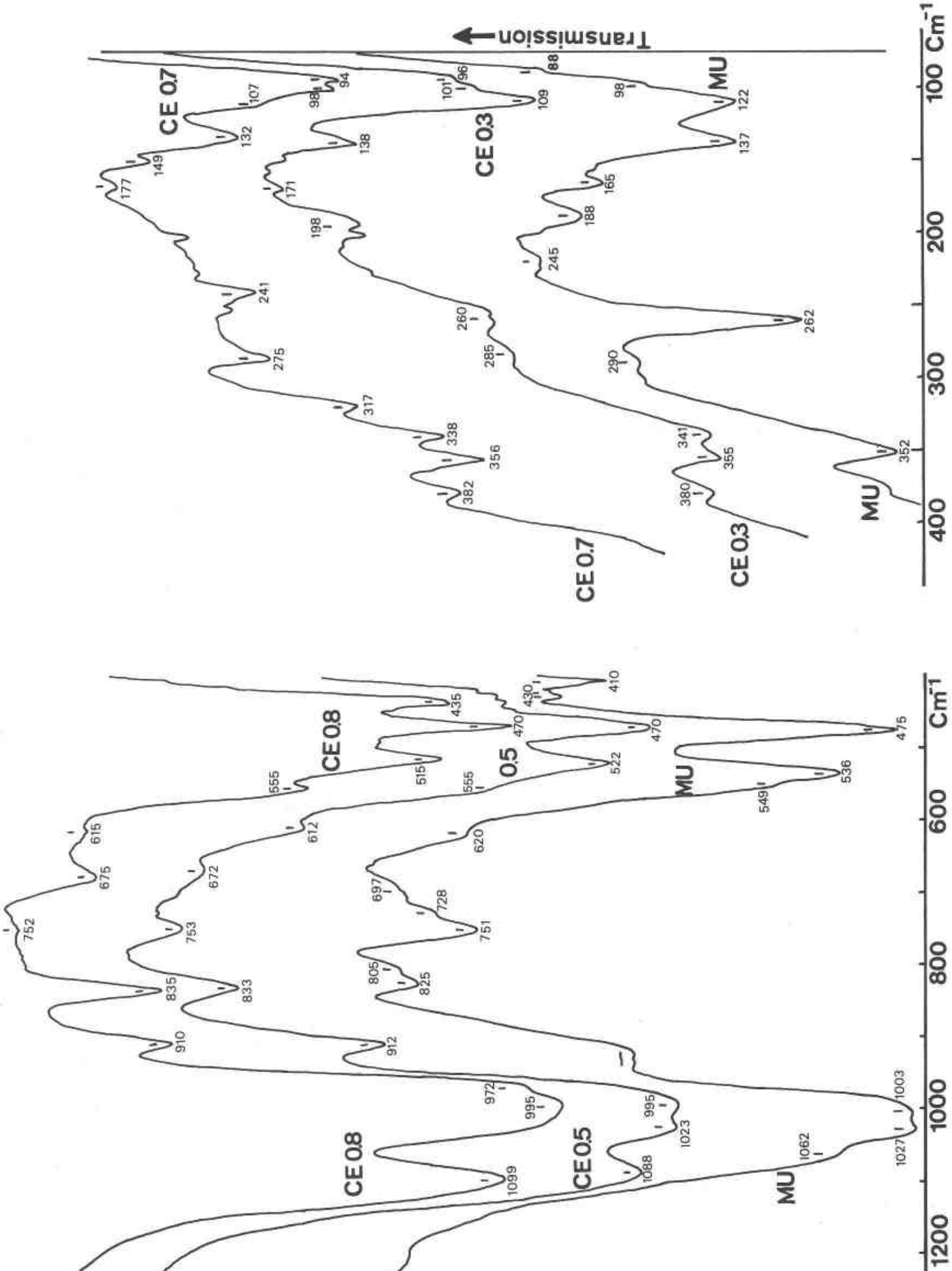

Fig. 1. Infrared spectra of several synthetic micas studied; MU = muscovite, CE 0.3 = 30 percent celadonite solid solution.

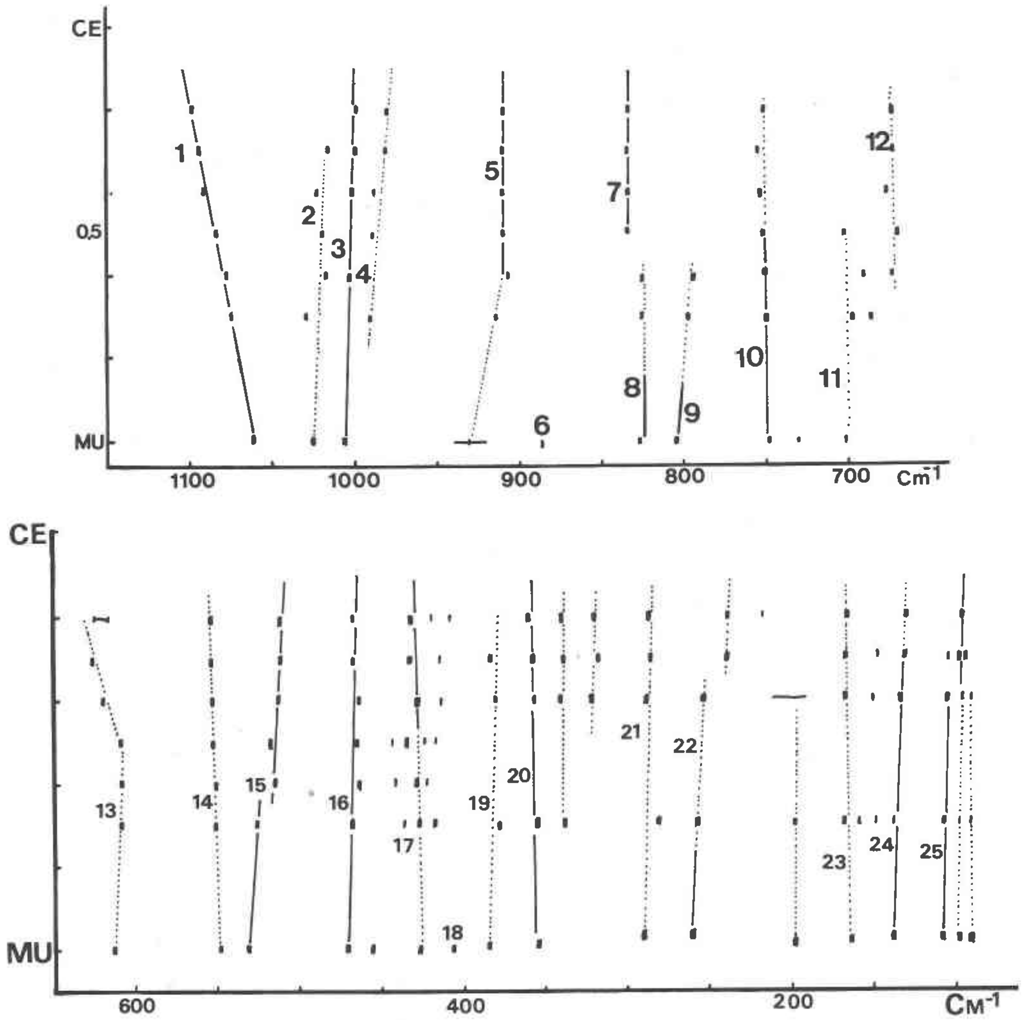

Fig. 2. Representation of the spectra used for the study. Numbers are arbitrarily given to major bands as wave number decreases. Solid lines indicate major intensities for the same vibration. Dotted lines indicate minor absorption. Assignment of atomic vibrations to each band can be found in Farmer (1974) or the text of this paper. MU = muscovite composition, CE = MgAl celadonite composition.

→ 2M. Band 6 becomes more apparent in the deuterated and 1M muscovite samples. This band (885 cm^{-1}) is also seen in synthetic non-ferrous smectites. It has been previously primarily attributed to Fe–OH vibrations (Farmer, 1974). Band 9 becomes more intense in the polymorphic sequence 1Md → 1M → 2M and is present in natural muscovites. It is considered to be a tetrahedral Al–O–Al vibration. Band 22 is very intense at the muscovite composition and decreases rapidly with celadonite substitution. It is found in other Al-dioctahedral minerals paragonite and margarite, as well as in magnesian clintonite. Bands 24 and 25, due to the vibration of the potassium ions, decrease in energy as the charge on the tetrahedral layer decreases.

Bands 1 and 14 were diminished by orientation of the mica flakes perpendicular to the infrared beam. Deuteration displaced bands 5, 7, 8 by amounts equal to ν OH/ν OD of 1.28 to 1.18 for band 5 and about 1.3 for bands 7 and 8. Bands 12 and 18 were displaced by deuteration also, but they could not be well identified due to overlap with other absorptions.

General observations

The assembled data from the interferometer traces indicate that there are three types of changes in the spectra of specific vibrations:

(1) A band will disappear with change of composition. This can be gradual or abrupt.

(2) A band will abruptly shift wave number at a

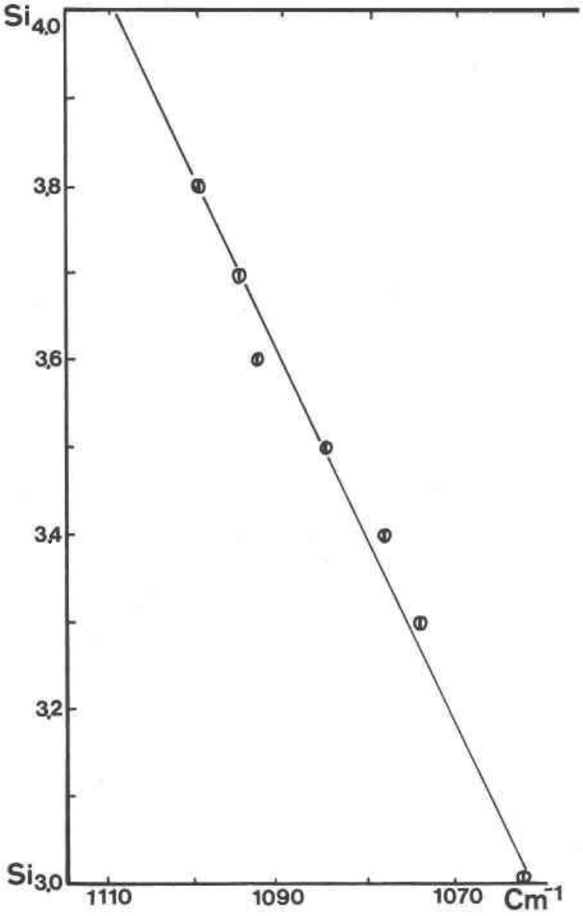

Fig. 3. Position of the a_1^1 Si–O apical band as a function of tetrahedral silicon content in the muscovite–celadonite series.

certain point in the compositional series. This is often accompanied by a multiplicity of bands in the spectrum in that region.

(3) A band will shift wave number in small increments which are directly related to the composition of the mica. Band widths or "sharpness" of the bands appear in general to be unaffected by compositional variation.

Si–O (apical) band

Let us consider the last case (3). In the spectra reported here, two bands shift very strongly with composition; both remain rather sharp, and thus neither indicate the introduction of new vibrations or significant coupling as the bands shift wave number. This behavior is generally called "single mode" shift (Chang and Mitra, 1968). Two such bands are numbered 1 and 15 in Figure 2. They occur at 1062–1100 cm^{-1} and 533–515 cm^{-1}. The first band (number 1) is most likely due to the silicon–apical oxygen tetrahedral stretch for the greatest part of its energy. Since the band does not appear to change its width as composition varies, one can probably assume that the Si for Al substitution in one tetrahedron does not greatly affect this vibrational mode in another tetrahedron by coupling, otherwise one would probably see more band-broadening. Figure 3 shows the position of the band as a function of composition as Al ions were added to or subtracted from the tetrahedral sites. A possible influence upon the vibrational energy of this Si–O stretch mode is the type of ion present in the octahedral sites which lie below the apical oxygen of the silica tetrahedron. Spectra of $MgFe^{3+}$ celadonite (Farmer, 1974) and tetrasilicic nickelous biotite [$KNi_{2.5}Si_4O_{10}(OH)_2$] given by Tateyama *et al.* (1976) suggest that the vibrational energy is essentially unmodified by the ionic occupation in the octahedral sites. The Si–O stretch mode is found at 1110 and 1115 cm^{-1} respectively for the other two minerals compared to an extrapolated 1108 cm^{-1} for pure MgAl celadonite. This constancy of "tetrahedral" vibrational energy has been found by the present author for synthetic Mg-, Fe-, Co-, Ni-biotites.

Observations of the wave number for Si–O apical stretching of several different mica mineral series indicate a somewhat varied behavior for various types of molecules. Figure 4 shows the wave number of the

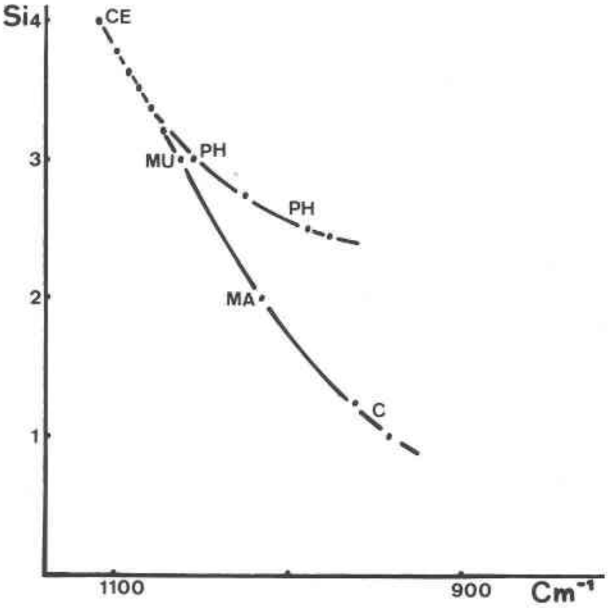

Fig. 4. Position of the a_1^1 Si–O apical band as a function of tetrahedral silicon content for synthetic muscovite–celadonite, the calcic micas margarite and clintonite (MA and C), and phlogopites (PH) (Farmer and Velde, 1973).

Si–O apical band as a function of Si occupancy in the tetrahedral positions for synthetic phengite, muscovite, margarite, two clintonites (calcic trioctahedral micas), and four phlogopites. The relation is rather linear from tetrasilicic mica through margarite, but the effect is exaggerated, as the silicon atoms fill less than half of the tetrahedral sites. Data for phlogopites show that the band shift occurs in the same manner for potassic trioctahedral micas, but the influence is greater per aluminum ion substituted in the tetrahedra. Here the effect becomes greatly exaggerated when more than one Al ion is present in the four possible sites. It seems then that the shift in wave number of the Si–O apical stretch vibration is different for different mica structures.

It would be surprising if the tetrahedral configuration varied in only one site. As can be seen in Figure 2, the other principal vibrations involving the basal oxygens shift to the opposite energy of the Si–O apical oxygen vibration (bands 2, 3, 4). These shifts could indicate different bond lengths or, as a result of change in bond length, the bond angles might differ, since these are Si–O–Si stretch modes involving more than one tetrahedral "edge."

The second band shift which is relatively simple is that of the vibrations for O–Si–O (number 15), where apical and basal oxygens are involved but where the Si atom does not vibrate. Here the energy and wave number decrease as the structure becomes tetrasilicic. This is the reverse of the Si–O apical band trend. It can be proposed that the Si–O basal bond angles increase enough to lower the energy of vibration.

Ordering

There are several bands shown in Figure 2 which do not follow a consistent "single mode" pattern of change from one end member to the other in the compositional series, most notably bands 5, 10, 11, 12, 13, and 17. In the case of band 5 a single mode wave number shift for a low intensity muscovite Al–OH libration absorption is abruptly changed to a sharp, more intense band with a constant wave number. This change occurs near 50 percent celadonite, indicating that ordering has occurred in the structure (Farmer, 1974). Ordering could also account for the sharp drop in intensity of the MgAlOH band (number 7), which is lost below 50 percent celadonite (band 8 is the Al–O apical vibration). It would appear then that ordering of the MgAl ions in the octahedral sites begins near 50 percent celadonite. The width of the AlOH band (number 5) at the muscovite composition suggests the possibility of two bands, which could indicate that not each octahedral Al has the same symmetry with respect to the OH ion—the two occupied octahedral sites are not symmetrically equivalent. Band 12 is due to an OH vibration, as seen in the deuterated sample. It becomes apparent at the intermediate composition of 30–50 percent celadonite and becomes a strong band at 80 percent celadonite.

The only major vibration identified here which could indicate whether or not there is tetrahedral ordering would be the Al–O–Si vibrational band at 750 cm^{-1} (band 10). There is a rapid decrease in intensity for this band between 50 and 60 percent celadonite compositions. This suggests that the tetrahedral sites are ordered to a certain extent between muscovite and 50 percent celadonite. They are no longer ordered at greater celadonite contents. This suggested tetrahedral ordering is the reverse trend noted for the octahedral sites, where Mg-Al ordering appears to begin at 50 percent celadonite and going toward higher celadonite contents. Band 17, very likely related to the Si–O network, increases greatly in intensity at >60 percent celadonite compositions. This might also indicate ordering in the tetrahedral network.

Band splitting

Several bands appear to behave as independent end members, *i.e.* become doublets at intermediate compositions between the poles in the mica series. This is the double mode behavior (Chang and Mitra, 1968). This is true for bands 2, 3, 4, the non-degenerate e_1^1 Si–O–Si mode. However, bands 17 and 20, which are attributed to lattice vibrational modes of the Si–O network, multiply at intermediate compositions. This splitting can be considered to be a result of non-equivalent sites being produced in the structure as composition changes (see White, in Farmer, 1974). More than one type of tetrahedral Si–O network seems to be present at intermediate compositions. It does not seem possible to try to predict whether or not the differences in the layers are long or short range, *i.e.* within one tetrahedral layer, between the two tetrahedral layers in the unit cell, or between different unit cells in the stacking sequence of the mica structure. Note that no band splitting or double mode behavior is observed for vibrations involving atoms in the octahedrally-coordinated layers in the 1200–80 cm^{-1} region.

Band 25, near 100 cm^{-1}, has been attributed to a potassium ion layer vibration by Farmer (1974). This band is evidently a doublet throughout the series

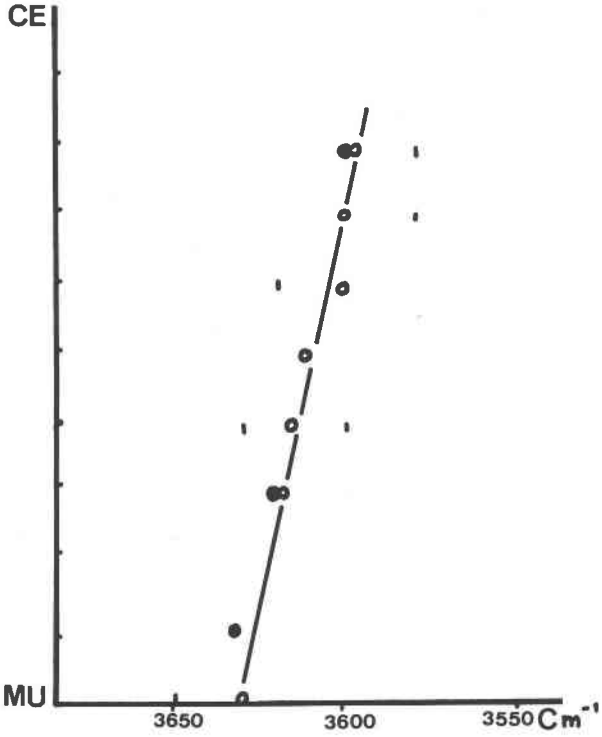

Fig. 5. OH stretch bands for the micas CE-celadonite to MU-muscovite. Bars represent minor intensity bands, open circles major intensity band (this study), and solid circles values reported in Farmer (1974).

studied, although not observed in this work. The most obvious explanation is that given by Tateyama *et al.* (1977), that the distorted hexagonal rings of oxygens ionically coordinated with the K^+ ion present two different bond-length distances and hence two vibrational energies. The sequence is continuous except for a slight displacement toward lower energy near 60 percent celadonite. The doublet is maintained from muscovite to the 80 percent celadonite mica.

This potassium vibration appears to change energy significantly depending upon the composition (and charge) of the adjacent tetrahedral layer. The band displacement appears double mode in type, although not enough spectra could be made to determine it well. In any event, it appears that the energy with which the potassium ion is held in the structure is different for muscovite and celadonite. Although the total compensating charge on the structure which balances the interlayer ion (+1) is the same in both cases, charge imbalance resulting from substitution in the octahedral (central) site seems to be less strongly exerted on the interlayer ion than that in the tetrahedral site. This should find confirmation by the fact that smectites with tetrahedral charge (beidellites) give lower swelling capacities than those of octahedral site charge (montmorillonites) for the same charge on the structure (Foster, 1953).

O–H stretching gives less information than for other silicates. Figure 5 shows that there are essentially two bands, 3650 minor intensity and 3630 major intensity, in muscovite and about 3600 major intensity and 3580 minor intensity for 80 percent celadonite. The minor intensity bands are not always apparent. However, the 40 percent celadonite sample shows all three bands. The major intensity band shifts in a regular manner as a function of mica composition; this suggests that the ordering of Mg–Al ions which affects the O–H libration band energy and sharpness does not influence the higher energy stretching mode band in the same way. Since the influence of MgAl and AlAl atom pairs on O–H stretching is undoubtedly quite different, due to the difference in charge (+5 and +6 respectively), the continuous displacement of the major band intensity energy should most likely be considered as a single mode type even though two satellite bands do appear.

Cell dimensions of micas

X-ray diffraction measurements made for the muscovite → 80 percent celadonite for 1M + 1Md mica polymorph aggregates indicate that the $c\sin\beta$ or c cell dimension does not vary in a regular manner with compositional change. However, (060) values for the series do show significant shifts with composition. Figure 6 shows the calculated b dimension [6 × (060)] as a function of mica composition. It appears that the rate of change in b is discontinuous near 50 percent celadonite. This cell dimension becomes much larger between 50 and 80 equivalent percent celadonite than between muscovite and 50 percent celadonite.

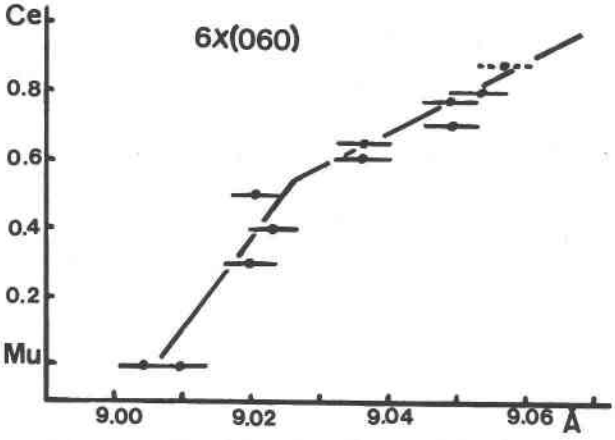

Fig. 6. b spacing = 6 × (060) of the synthetic micas.

Discussion

The infrared spectra reported here demonstrate the importance of using a closely-spaced compositional series in order to assess the various shifts in wave number for the different vibrational bands in the spectra. Based upon these data, several general observations can be made concerning the mica structures between muscovite and celadonite compositions:

(1) Ordering is probable in the octahedrally-coordinated ion sites between celadonite and about 50 percent celadonite composition. This is suggested from libration bands of OH groups and from cell dimensions.

(2) Ordering on tetrahedral sites is possible, but different types of sites at intermediate compositions between muscovite and celadonite are probable. This suggests inhomogeneity at some scale between the various tetrahedrally-coordinated layers.

(3) The single-mode shift of the a_1^1, Si–O apical vibration near 1100 cm^{-1} seems to characterize the type of mica substitution, be it di- or trioctahedral mica. This band might be useful as diagnostic for distinguishing a type 2:1 structure in a mixed-layered mineral edifice.

An observation which is rather striking for these minerals (muscovite–celadonite) and phyllosilicates in general is the relative independance of the tetrahedrally-coordinated layers and the octahedrally-coordinated ions. It appears that octahedral-ion–OH vibrations are common, but no evidence is forthcoming for a tetrahedral-oxygen–octahedral-ion vibration. The basic edifice is the tetrahedral ion–oxygen complex, where interlayer ions and octahedrally-coordinated ions and OH appear to vibrate independently. In the micas investigated, the octahedral-ion species seems to affect but little the Si–O network. More careful correlation of lattice vibrations will give better information concerning this idea.

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