Synthesis and Swelling Properties of Fluorine Micas with Variable Layer Charges

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(Received September 25, 1984)

Synopsis. A series of tetrasilicic Na-micas with variable layer charges (x) between x=1 and x=0.32, $Na_xMg_{3-x}Li_x(Si_4O_{10})F_2$, was synthesized. The expansibility of the synthesized Na-micas upon swelling increased with decreasing layer charge.

Some of the synthetic fluorine micas are swellable with water.[1] However, detailed studies on the effect of the magnitude of layer charge upon the expansibility of fluorine micas have been lacking. The layer charge results generally from positive charge deficiencies in both tetrahedral and octahedral sheets. The value of layer charge, which is expressed as the net negative charge per formula unit, is an important parameter for the classification of layer silicates. Na-taeniolite[2] $NaMg_2Li(Si_4O_{10})F_2$ is a representative species of these synthetic expansible fluorine micas. In this note, the substituted analogues of Na-taeniolite with decreasing layer charge, $Na_xMg_{3-x}Li_x(Si_4O_{10})F_2$ ($1 \geqq x \geqq 0.1$), are synthesized to examine the limit of variability in layer charge and also to elucidate the correlation between the magnitude of layer charge and the swelling properties. In this series the layer charge results from charge deficiency only in octahedral sheet and its value is the same as the x-value.

Raw materials used were chemically pure NaF, MgO, MgF_2, LiF, and SiO_2. Raw materials mixed in proportions corresponding to the formula described above, were sealed in platinum tubes and heated at 1420 °C for 2 h. The temperature was then lowered at a rate of 2—3 °C per minute to 800 °C and the tube was taken out of the furnace to cool in air. The crystal aggregates thus obtained were powdered and purified by sedimentation in distilled water. The products were investigated by powder X-ray diffractometry, electron scanning microscopy, and infrared spectroscopy. The chemical analysis was done for Na and Li by a flame-emission method after the purified samples were dissolved in HF–H_2SO_4 solutions. The layer charge for micas is determined from the content of interlayer Na. The infrared spectra were measured by a KBr pellet method. Swelling of the micas was investigated by an X-ray diffraction method through the measurements of basal spacing (d_{001}) of the samples wetted with water, ethylene glycol, or glycerol.

The batches with the x-value of 1.0—0.6 were melted at 1420 °C, whereas the batches with the x-value smaller than 0.6 was not melted but sintered. The size of mica crystals decreased with decreasing x-value. X-Ray diffraction patterns indicated that only mica was formed from the batches having the x-value of 1.0—0.8. However, the traces of coexistent minerals such as fluor-richterite, α-cristobalite, and α-tridymite were observed for the batches having the x-value of 0.7—0.5, and their contents were not negligible at x=0.4—0.1.

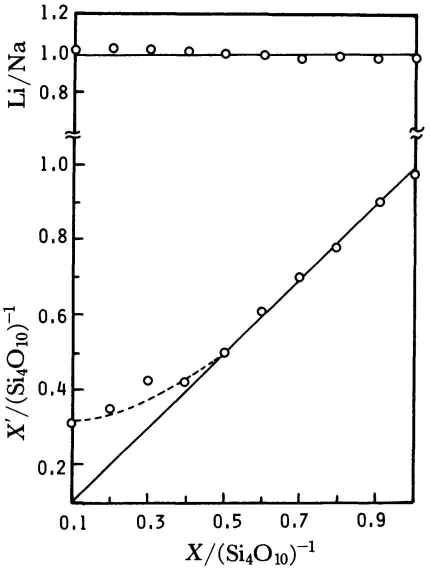

Fig. 1. The determined layer charge (x') and Li/Na mole ratio of synthesized Na-micas plotted against the ideal layer charge (x) calculated from batch composition.

The infrared spectra of the micas showed that the main absorption band at 980 cm^{-1} for x=1.0, which is assigned to e_1^1 mode of Si_2O_5 group,[3] gradually shifted towards higher frequencies with decreasing x-value although the shifting was not observed below x=0.4. On the other hand, another main band at 1110 cm^{-1}, which is assigned to a_1^1 mode of Si_2O_5 group,[3] shifted reversely to lower frequencies with decreasing x-value. The linear relationship is obtained between x-values and wavenumber ($\tilde{\nu}$) in the range x=1.0—0.5 as follows:

$$e_1^1 ; \quad \tilde{\nu} = 980 + 28x \ (\mathrm{cm}^{-1})$$

$$a_1^1 ; \quad \tilde{\nu} = 1110 + 40x \ (\mathrm{cm}^{-1})$$

This implies that the tetrahedral lattice vibrations are affected by the magnitude of layer charge and/or the changes of octahedral and interlayer compositions.

Figure 1 shows the relationship between the determined layer charge (x') of the synthesized micas and the ideal layer charge (x) calculated from batch composition. The observed mole ratio of Na and Li in mica crystals is also plotted against the x-value in Fig. 1. The ratios of Na to Li are 1.00±0.03 corresponding to the theoretical value of 1.00 throughout the series. The dotted line shows the variation of x'-values, while the full line shows that of x-values. If the synthesis was fully successful, the x'-value should be equal to the x-value. As seen in Fig. 1, the curve of x'-values almost agrees with that of x-values in the range of x=1.0—0.4. However, the x'-value deviates from the x-value below x=0.3, converging to about

Table 1. Basal spacings[a)] of Na-micas upon water, ethylene glycol, and glycerol solvation

	$x/(\mathrm{Si_4O_{10}})^{-1}$	1.0	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1
$\frac{d_{001}}{\text{Å}}$	Water	15.1 (12.2)	15.1 (12.2)	15.1	15.1	18.4 (15.1)	18.4 (15.1)	f.s.[b)] (18.4)	f.s.	f.s.	f.s.
	Ethylene glycol	12.3	12.3	12.3 (16.7)	12.3 (16.7)	16.7 (12.3)	16.7 (12.3)	16.7	16.7	16.7	16.7
	Glycerol	12.7	12.6	14.3 (12.6)	14.2 (12.6)	14.5	14.3 (17.7)	18.0 (14.3)	18.0	17.9	17.8

a) The basal spacing of minor phase is shown in parenthesis. b) f.s. shows free swelling.

x'=0.32 with decreasing x-value. Although solid state reaction was attempted repeatedly for the samples of x=0.2—0.1 at 1450 °C for prolonged times in a sealed platinum tube, no x'-value lower than 0.32 was found. These results suggest that the micas having the desired compositions precipitated in the range x=1.0—0.4 and that there is a limitation in the variability of layer charge for the Na-micas. At present it is not clear whether this limitation originates from synthetic conditions or crystallochemical factors such as the weakening of the interlayer bonding in the mica structure.

Table 1 gives the basal spacings of the Na-micas which were wetted with water, ethylene glycol, and glycerol for at least 2 h. The basal spacings of minor phases simultaneously observed are also shown in parentheses. In contact with water, all the micas of the series with layer charge lower than 0.5 exhibited so-called free swelling: X-ray patterns show diffuse scattering at low angles. It is clearly seen in Table 1 that the Na-micas undergo either free swelling or limited swelling according to the magnitude of layer charge. Our study shows also that there is a critical point at the layer charge where the maximum basal spacing is limited to either 15.1 Å of double-layer hydrate or 18.4 Å of three-layer hydrate state. The coexistence of two hydrate phases can be explained by the heterogeneity of layer charge in successive layers and also by the kinetics of swelling. Accordingly, the actual layer charge obtained from chemical analysis should be considered as the mean value of the successive layers. In contact with ethylene glycol, the formed complexes gave the basal spacing ranging from 12.3 Å to 16.7 Å, suggesting that the arrangement of ethylene glycol molecules in the interlayer regions is dependent upon the magnitude of layer charge. The basal spacings of 12.3 Å and 16.7 Å correspond to a single-layer[4)] and a double-layer complex,[5)] respectively. The boundary between the double-layer complex and single-layer one appears at about x=0.7. In contact with glycerol, the complexes gave the basal spacing ranging from 12.7 Å (single-layer) to 18.0 Å (double-layer). The 14.2 Å phase may also correspond to a single-layer complex with a different arrangement of glycerol molecules. The boundaries between the complexes of glycerol appear at the layer charge of x=0.9 and x=0.5.

It is concluded from these results that the expansion of basal spacings in the expansible fluorine micas becomes greater as the layer charge decreases whatever the solvation is. This can be attributed to the weakening of interlayer coulombic force resulted from the decrease of layer charge and also to the increase of the density of interlayer vacancies.

References

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