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# SYNTHESIS AND SWELLING OF Sr-FLUORINE MICAS

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A series of Sr-micas corresponding to the general formula $SrMg_2Li_x(Al_xSi_{4-x}O_{10})F_2$ ( x=1.0-0.5 ) were synthesized and swelling with water was observed for the micas ( $x \leqq 0.7$ ). The difference in swelling tendencies of Sr-micas can be ascribed to the distribution of positive charge deficiency and the degree of distortion in tetrahedral sheets.

A wide variety of isomorphically substituted fluorinemicas have been synthesized by melting or solid state reaction of suitable batch materials.1) Some of them have been found to exhibit swelling properties with water. Li-taeniolite[$LiMg_2Li(Si_4O_{10})F_2$] and Na-taeniolite [$NaMg_2Li(Si_4O_{10})F_2$] are representative species of these expandable fluorinemicas, and swelling and dehydration characteristics were studied by the authors.2,3) Swelling is an important phenomenon, associated with intercalation and cation exchange of layer-silicates. In attempting to elucidate the origins of swelling in these water-swellable fluorinemicas, a successive series of hypothetical Sr-fluorinemicas corresponding to the general formula $SrMg_2Li_x(Al_xSi_{4-x}O_{10})F_2$ [ where x= 1.0,0.9,0.8,0.7,0.6, or 0.5], were tried to synthesize, and swelling of these Sr-series micas is investigated in connection with the distribution and degree of positive charge deficiency in mica structure. The role of the interlayer cation $Sr^{2+}$ on the instability of interlayer structure is also discussed with relation to the structural deformation4) of interlayer polyhedra.

Raw materials used were chemically pure $SrF_2$, MgO, $Al_2O_3$, $SiO_2$, and $Li_2CO_3$. Well-mixed raw materials, which were in correct proportions corresponding to the formula described above, were sealed in platinum crucibles and melted at 1400 °C for 2 h. The temperature was then lowered at 2 - 3 °C per minute to 800 °C when the crucible was taken out of the furnace and cooled in air. The crystal aggregates thus obtained were powdered and sieved for purification. The confirmation of these Sr-micas was carried out by the methods of X-ray diffraction, chemical analysis and infrared spectroscopy. Chemical analysis was done by flame-emission method for Sr and Li,5) and by atomic absorption method for Mg6) and Al,7) using $N_2O-C_2H_2$ flame, after the purified Sr-micas were dissolved in $HF-HNO_3$ solutions. The corrections were made for the interference of coexistent elements. The infrared spectra were measured by KBr pellet method. Swelling and Dehydration characteristics were investigated by X-ray diffraction, DTA and TG methods.

The larger flakes of mica crystals were obtained as the x-value of batches was increased. The X-ray diffraction patterns indicated that the every synthesized sample contained the predominant phase of mica and traces of norbergite[$Mg_3SiO_4F_2$]

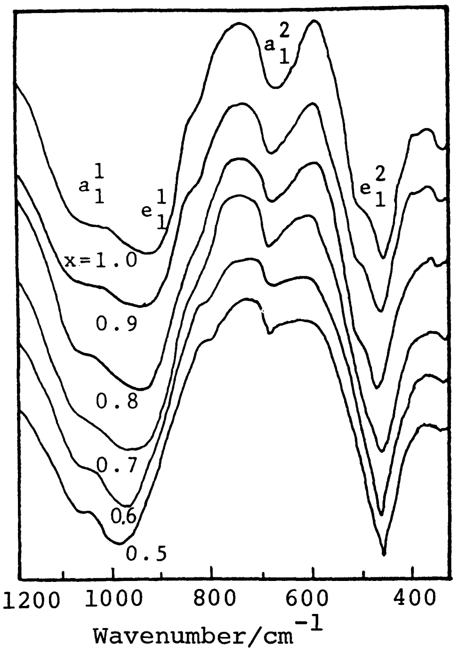

Fig.1. Infrared spectra of Sr-micas.

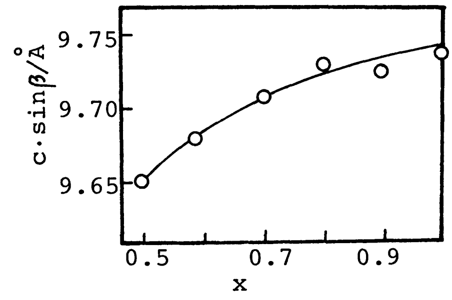

Fig.2. The variation of basal spacing shown against the x-value of Sr-micas.

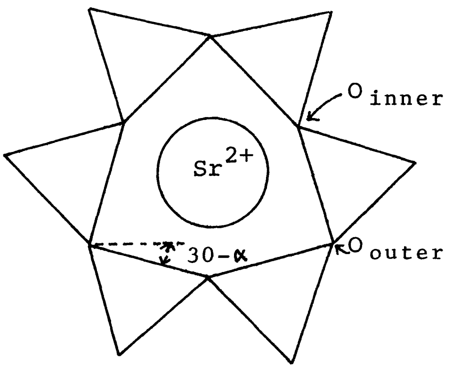

Fig.3. Schematic view along c* illustrating the arrangement of silica tetrahedra about the strontium cation.

and $SrF_2$. The calculated formula from the results of chemical analysis, for example, is expressed as $Sr_{0.97}Mg_{2.01}Li_{0.84}(Al_{0.88}Si_{3.12}O_{10})F_2$ for x=0.9 and $Sr_{0.99}Mg_{2.01}Li_{0.48}(Al_{0.56}Si_{3.44}O_{10})F_2$ for x=0.6, respectively, based on the assumption of Si+Al=4.00 and O+F=12. These results support that actual formulas of the synthesized Sr-micas are approximated to batch formulas throughout the series. Thus syntheses of Sr-fluorinemicas were substantially confirmed.

The infrared spectra of the Sr-micas are shown in Fig.1. The absorption bands for x=1.0 at 1083, 939,688 and 467 cm$^{-1}$ might be assigned to $a_1^1$, $e_1^1$, $a_1^2$ and $e_1^2$ vibration modes of $Si_2O_5$ group,[8] respectively. The shift of $e_1^1$-band to a higher frequency with decreasing x-value clearly shows the effect of isomorphic substitutions, suggesting that the structure or the symmetry of $Si_2O_5$ group changes with the substitutions. The absorption band or the shoulder at 835-815 cm$^{-1}$ can be assigned to the vibration of Al-O-Si.[8] The infrared spectrum of Sr-mica changes very sensitively with the amount of substitutions.

Figure 2 shows the relationship between the basal spacing and the x-value of Sr-micas. The basal spacing(c·sinβ) changes considerably from 9.739 Å(x=1.0) to 9.676 Å(x=0.5) due to the shortening of the mean (Si,Al)-O distance, whereas b-dimension slightly changes from 9.009 Å(x=1.0) to 9.032 Å(x=0.5). The smaller b-dimension of Sr-mica, compared with those of trisilicic micas, suggests that the degree of distortion in tetrahedral sheets may be extremely high, and that the coordination number of Sr cation is 6 rather than 12 of the ideal mica structure as shown in Fig.3. That is, the interlayer Sr cation is coordinated by 6 inner basal oxygens and 6 outer basal oxygens, which form two octahedra penetrating with each other.

The degree of distortion in tetrahedral sheets is expressed in terms of a tetrahedron rotation angle(α).[4] By the equation[9] $\alpha=\cos^{-1}(b/2\sqrt{3}e_b)$, where b is a measured b-dimension and $e_b$ is a basal O-O distance, α-values were estimated as 13.2° for x=1.0 using the $e_b$-value(2.671 Å) of F-phlogopite[$KMg_3(AlSi_3O_{10})F_2$][9] and as 9.6° for x=0.5 using the $e_b$-value (2.644 Å), which is the mean value for the $e_b$-value of F-phlogopite and that of taeniolite[10] [$KMg_2Li(Si_4O_{10})F_2$]. The α-value of Sr-micas thus obtained is a very larger one, which varies with the x-value. The larger α-value, which means the higher degree of distortion in tetrahedral sheets, should be attributed not only to the dimensional misfit between tetrahedral and octahedral sheets as can be generally seen but also to the small size and field strength of the interlayer $Sr^{2+}$cation, since such larger values of α can not be explained merely by the tetrahedral-octahedral sheet misfit. It is reasonable that the α-value decreases with the decrease of x-value since the shortening of a mean (Al,Si)-O bonding distance occurs with Si-for-Al substitutions, resulting in the decrease of misfit. The degree of distortion in tetrahedral sheets, which is closely related to the interlayer structure, seems to have an important role on the swelling of micas because the coordination of the interlayer cation depends on the magnitude of α. When an interlayer cation is too small to fit into the interlayer polyhedron of basal oxygens and the stable coordination around the interlayer cation is not attained by the distortion of tetrahedral sheets, the interlayer structure should be in an unstable state which is favourable for swelling. That is, it is likely that the smaller α-value is favourable for swelling. The role of interlayer cation $Sr^{2+}$ will be further discussed below in connection with the charge balancing.

Figure 4 shows X-ray diffraction patterns of Sr-series micas wetted with water in the (001) reflection region. Any crystalline swelling states were not observed for the Sr-micas of x=1.0-0.8, however, $d_{001}$=12.3 Å phase of single-layer hydrated state appears at x=0.7 and $d_{001}$=15.2 Å phase of double-layer hydrated state appears at x=0.5 as shown in Fig.4. The results indicate that the content of each hydrated phase as well as the degree of hydration stage increase with the decrease of x-value. The coexistence of different hydrated phases at the same time may be attributed to the compositional inhomogeneity throughout the successive layers of mica crystals and also to the kinetics of hydration. The single-layer hydrated state for x=0.5 is stable in air and the sample, equilibrated in air at 20 °C and R.H.=40%, shows the endothermic peak at about 145 °C, which can be attributed to the dehydration of interlayer water molecules.

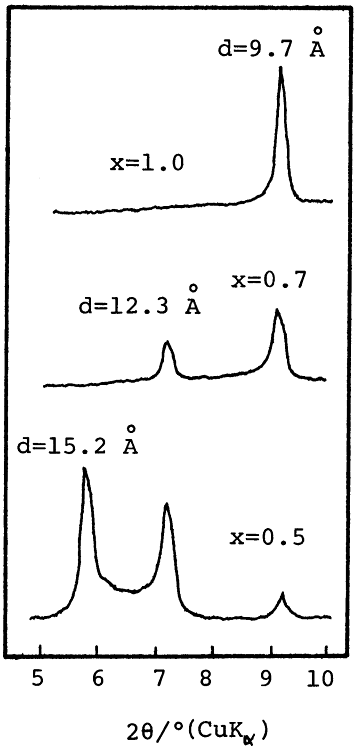

Fig.4. X-Ray diffraction patterns of Sr-micas wetted with water.

The similarlity in ionic radius[11] between $Sr^{2+}$ (1.18 Å) and $Na^+$(0.99 Å) suggests that the Sr-mica may have potentials to swell with water. However, the differences were observed in the swelling of Sr-micas, and seemed to arise from the variation in the distribution and the degree of positive charge deficiency as well as the degree of distortion in tetrahedral sheets.

The so-called layer charge is ideally -2.00 for the Sr-series micas, which is compensated by the positive charge of an interlayer $Sr^{2+}$ cation. Positive charge deficiency results from both octahedral and tetrahedral sheets in these Sr-micas. The variation in the distribution and degree of charge deficiency

Table 1. Distribution of positive charge deficiency[a)] for each sheet and its contribution (%) to the layer charge in Sr-micas [$SrMg_2Li_x(Al_xSi_{4-x}O_{10})F_2$]

| x | 1.0 | 0.9 | 0.8 | 0.7 | 0.6 | 0.5 |
|---|---|---|---|---|---|---|
| Tetrahedral sheet[a)] | 1.0 | 0.9 | 0.8 | 0.7 | 0.6 | 0.5 |
| (%) | 50 | 45 | 40 | 35 | 30 | 25 |
| Octahedral sheet[a)] | 1.0 | 1.1 | 1.2 | 1.3 | 1.4 | 1.5 |
| (%) | 50 | 55 | 60 | 65 | 70 | 75 |

a) Positive charge deficiency is shown per formula unit.

for each sheet is shown in Table 1. Replacement of $Mg^{2+}$ by $Li^+$ and vacancy in octahedral sheets results in incomplete neutralization of negative charges on the apical oxygens ($O_a$), whereas substitution of Al for Si in tetrahedral sheets results in incomplete neutralization of negative charges mainly on the basal oxygens ($O_b$). The layer charge is a sum of the tetrahedral and octahedral negative charge. The change in the distribution of positive charge deficiency on the tetrahedral and octahedral sheet is clearly seen in Table 1. The contribution of charge deficiency to the layer charge for the octahedral sheet increases from 50% to 75% as the x-value decreases from 1.0 to 0.5.

The localization of charge deficiency on the octahedral sheet, compared with that on the tetrahedral sheet, seems to result in weakening the interlayer bonding of silicate layers, since in this case the negative charge is postulated to localize on the apical oxygens, which is far distant from the interlayer cation $Sr^{2+}$, rather than on the basal oxygens. On the other hand, the tetrahedral charge deficiency results in rather strong bondings between Sr and $O_b$, increasing the stability of the interlayer region. In this case swelling should be difficult as seen for Sr-micas having larger x-values. Accordingly, it is concluded that the swelling occurs in Sr-mica having a lower x-value, owing to the change in the distribution of charge deficiency and the interlayer structure. The effect of octahedral vacancies on expansibility of fluorinemicas should be also discussed, however, further studies are necessary.

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