SYNTHETIC RESEARCH OF VARIOUS KINDS
OF MICAS (SUMMARY)*

Nobutoshi DAIMON

Department of Applied Chemistry

Various kinds of micas were prepared synthetically by substituting tetrahedral aluminum in the fluor-phlogopite F_2KMg_3 ($AlSi_3O_{10}$) by zinc,[1] beryllium,[1] boron,[1] cobalt[3] or iron;[2] a part of octahedral magnesium by iron,[2] manganese,[4] cobalt,[3] nickel,[4] lithium[5] or zinc[6]; and 12-fold coordinated potassium by sodium,[1] calcium,[5] strontium[5] or barium[5] respectively.

Batch compositions are shown in Table 1. The melting temperatures of batches are listed in the table. The batch materials were "C.P." grade. The chemical formulae of the produced micas and of some natural micas[7] are shown in Table 2. Their optical constants are shown in Table 3.

The structure of phlogopite crystal is composed of three kinds of layers:

$$(1) \ (SiO_4), \ (AlO_4), \quad (2) \ (MgO_6), \quad (3) \ (KO_{12}).$$
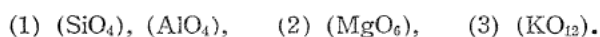
The K-O bond is said to have 80% ionic character, the Mg-O 73%, and the Si-O 50% according to L. Pauling.[8] The Si-O bond has sp^3 hybrid bond character and some double bond character besides the ionic one. The K-O bond may be considered to have an ideal ionic character.

TABLE 1

	Batch composition	Melting Temp. °C
1. Zn-Mica	0.5 K_2SiF_6, 3 MgO, 0.5 ZnO, 3 SiO_2	1,250
2. Fe-Mica	0.5 K_2SiF_6, 3 MgO, 0.5 FeO, 3 SiO_2	1,350
3. Na-Mica	0.5 Na_2CO_3, 1.5 MgO, 1.5 MgF_2, 0.5 Al_2O_3, 3 SiO_2	1,300
4. B-Mica	0.5 K_2SiF_6, 3 MgO, 0.5 B_2O_3, 2.5 SiO_2	1,250
5. Co^p-Mica	0.5 K_2SiF_6, 2.75 MgO, 0.08 Co_3O_4, 0.5 Al_2O_3, 2.5 SiO_2	1,400
6. Co^b-Mica	0.5 K_2SiF_6, 2 MgO, 0.03 Co_3O_4, 0.5 B_2O_3, 2.5 SiO_2	1,200
7. $Ba_{0.5}$-Mica	0.5 $BaCO_3$, 1.5 MgO, 1.5 MgF_2, 0.5 Al_2O_3, 3 SiO_2	1,400
8. BaLi-Mica	BaF_2, 2 MgO, 0.5 Li_2CO_3, 0.5 B_2O_3, 3 SiO_2	1,150
9. SrLi-Mica	SrF_2, 2 MgO, 0.5 Li_2CO_3, 0.5 B_2O_3, 3 SiO_2	1,160
10. CaLi-Mica	CaF_2, 2 MgO, 0 5 Li_2CO_3, 0.5 B_2O_3, 3 SiO_2	1,080
11. Ni-Mica	0.5 K_2SiF_6, 2.75 MgO, 0.25 $NiCO_3$, 0.5 Al_2O_3, 2.5 SiO_2	1,380
12. Mn-Mica	0.5 K_2SiF_6, 1.5 MgO, 1.5 MnO, 0.5 Al_2O_3, 2.5 SiO_2	1,350
13. Fe^{++}-Mica	0.5 K_2SiF_6, 1.5 MgO, 1.5 FeO, 0.5 Al_2O_3, 2.5 SiO_2	1,350
14. $FeAl^{+++}$-Mica	0.5 K_2SiF_6, 2.75 MgO, 0.08 Fe_2O_3. 0.5 Al_2O_3, 2.5 SiO_2	1,380
15. Fe^{+++}-Mica	0.5 K_2SiF_6, 3 MgO, 0.5 Fe_2O_3, 2.5 SiO_2	1,300
16. Zn^2-Mica	0.5 K_2CO_3, 1.5 MgO, 1.5 MgF_2, ZnO, 3.5 SiO_2	1,260

TABLE 2

		Chemical formula
1.	Zn-Mica	$(F_{1.92}O_{0.08})K_{0.96}Mg_{2.57}Fe_{0.04}(Al_{0.18}Zn_{0.40}Si_{3.42}O_{10.00})$
2.	Be-Mica	$(F_{1.94}O_{0.06})K_{0.91}Mg_{2.95}Fe_{0.02}Al_{0.02}(Be_{0.47}Al_{0.04}Si_{3.49}O_{10.00})$
3.	Na-Mica	$(F_{1.78}O_{0.22})K_{0.07}Na_{0.88}Mg_{3.02}Fe_{0.01}Al_{0.04}(Al_{0.98}Si_{3.02}O_{10.00})$
4.	B-Mica	$(F_{1.98}O_{0.02})K_{0.97}Mg_{3.03}Fe_{0.02}(Al_{0.35}B_{0.62}Si_{3.00}O_{10.00})$
5.	Co^p-Mica	$(F_{1.78}O_{0.22})K_{0.95}Mg_{2.99}Fe_{0.04}Co_{0.10}(Al_{1.10}Si_{2.91}O_{10.00})$
6.	Co^b-Mica	$(F_{1.81}O_{0.19})K_{0.94}Mg_{2.85}Al_{0.21}(Al_{0.17}B_{0.23}Co_{0.33}Si_{3.27}O_{10.00})$
7.	$Ba_{0.5}$-Mica	$(F_{1.94}O_{0.06})K_{0.19}Ba_{0.41}Mg_{3.02}Fe_{0.02}(Al_{0.97}Si_{3.02}O_{10.00})$
8.	BaLi-Mica	$\{F_{1.63}O_{0.37}\}K_{0.03}Ba_{1.00}Li_{0.77}Fe_{0.01}Mg_{1.43}Al_{0.17}(B_{0.25}Al_{0.72}Si_{3.02}O_{10.00})$
9.	SrLi-Mica	$(F_{1.58}O_{0.42})K_{0.03}Sr_{1.00}Li_{0.94}Fe_{0.02}Mg_{2.11}Al_{0.06}(B_{0.31}Al_{0.76}Si_{2.96}O_{10.00})$
10.	CaLi-Mica	$(F_{1.57}O_{0.43})K_{0.08}Ca_{0.94}Li_{0.86}Fe_{0.01}Mg_{2.17}(B_{0.22}Al_{0.77}Si_{3.01}O_{10.00})$
11.	Ni-Mica	$(F_{1.77}O_{0.23})K_{0.90}Mg_{2.86}Ni_{0.16}Fe_{0.01}(Al_{0.99}Si_{3.00}O_{10.00})$
12.	Mn-Mica	$(F_{1.92}O_{0.08})K_{0.93}Mg_{2.64}Mn_{0.37}Fe_{0.01}(Al_{0.99}Si_{2.97}O_{10.00})$
13.	Fe^{++}-Mica	$(F_{1.63}O_{0.37})K_{0.99}Mg_{2.62}Fe^{++}_{0.41}Al_{0.05}(Al_{0.88}Si_{3.12}O_{10.00})$
14.	FeAl-Mica	$(F_{1.77}O_{0.23})K_{0.90}Mg_{2.80}Fe^{++}_{0.14}Fe^{+++}_{0.23}(Al_{1.08}Si_{2.88}O_{10.00})$
15.	Fe^{+++}-Mica	$(F_{1.80}O_{0.20})K_{0.95}Mg_{2.76}Fe^{++}_{0.17}Fe^{+++}_{0.03}(Fe^{+++}_{0.57}Al_{0.32}Si_{3.11}O_{10.00})$
16.	Zn^2-Mica	$F_{2.0}K_{1.0}Mg_{2.9}Zn_{0.2}(Zn_{0.2}Al_{0.8}Si_{3.0}O_{10.00})$
17.	K-Phlogopite	$(F_{1.57}O_{0.43})K_{1.01}Mg_{3.07}Al_{0.09}(Al_{1.01}Si_{2.99}O_{10.00})$
18.	Natural phlogopite	$[F_{1.19}O_{0.26}(OH)_{0.55}]K_{0.78}Na_{0.05}Ca_{0.01}Mg_{2.80}Fe^{++}_{0.54}Fe^{+++}_{0.02}Al_{0.15}(Al_{0.98}Si_{3.02}O_{10.00})$
19.	Natural biotite	$[O_{0.41}(OH)_{1.59}]K_{0.73}Na_{0.29}Ca_{0.06}Mg_{1.64}Fe^{++}_{0.79}Fe^{+++}_{0.10}Ti_{0.02}Al_{0.39}(Al_{1.12}Si_{2.88}O_{10.00})$
20.	Natural muscovite	$[O_{0.02}(OH)_{1.98}]K_{0.88}Na_{0.14}Ca_{0.01}Mg_{0.09}Fe^{++}_{0.11}Fe^{+++}_{0.26}Ti_{0.05}Al_{1.71}(Al_{0.91}Si_{3.09}O_{10.00})$

A part of Fe in 6-fold coordination in the chemical formulae may be put into 4-fold coordination.

TABLE 3

		Refractive index			Optical angle		Pleochroism		
		α	β	γ	2 E	2 V	X	$<$	Y = Z
1.	Zn-Mica	1.524	1.553	1.553	20	13	—		—
2.	Be-Mica	1.501	1.516	1.516	—	—	—		—
3.	Na-Mica	1.510	1.533	1.533	30	20	—		—
4.	B-Mica	1.503	1.523	1.523	35	24	—		—
5.	Co^p-Mica	1.519	1.547	1.547	22	14	almost colourless		pink
6.	Co^b-Mica	1.527	1.556	1.557	22	14	blue		blue
7.	$Ba_{0.5}$-Mica	1.517	1.546	1.546	30	20	—		—
8.	BaLi-Mica	1.549	1.586	1.587	—	—	—		—
9.	SrLi-Mica	1.527	1.555	1.556	20	13	—		—
10.	CaLi-Mica	1.519	1.546	1.547	—	—	—		—
11.	Ni-Mica	1.512	1.537	1.539	20	13	almost colourless		greenish yellow
12.	Mn-Mica	1.514	1.544	1.545	36	23	yellow		brown
13.	Fe^{++}-Mica	1.515	1.539	1.540	16	10	almost colourless		greenish black
14.	FeAl-Mica	1.516	1.543	1.543	18	16	almost colourless		brown
15.	Fe^{+++}-Mica	1.543	1.567	1.568	18	11	almost colourless		brown

(1) On the Isomorphous Substitution of Synthetic Mica

Principal factors of isomorphous substitution of a cation in mica crystals are (1) the size of ion, (2) hybrid bond character, and (3) temperature-dependence of coordination number.

As well known, the coordination number of a cation is determined by its size, or to be more specific, by the ratio of the radius of a cation to that of an anion quite geometrically in the ionic crystal. 12-fold coordinated potassium ion can be

substituted by a large cation such as of sodium, calcium, strontium or barium; octahedral magnesium by zinc or lithium; and tetrahedral aluminum by beryllium or boron.

Six equivalent bond orbitals (i.e. d^2sp^3 hybrid bond orbitals) can be formed, when only two d orbitals are available for the combination with s- and p-orbitals. These hybrid bond orbitals have their bond directions towards the corners of a regular octahedron. From the above theoretical consideration, it is concluded that cobalt, iron, manganese, and nickel should take the octahedral coordination in mica. The Be-O, the B-O, the Al-O, and the Zn-O bond have the same sp^3 hybrid bond character as the Si-O bond.

Aluminum in phlogopite could be substituted by zinc, cobalt or ferric iron, as shown in the synthetic experiments. It is assumed that the increase of the volume of oxide at high temperatures may be mainly due to the apparent increase of the volume of oxygen ion and that is why a cation such as of zinc, cobalt or ferric iron can take 4-fold coordination at high temperatures, while a higher coordination is expected to be stable at the room temperature.

In a sodalime glass containing nickel oxide, for example, it can be demonstrated that the quenched glass has a definite purple shade (NiO_4 groups impart a purple color in glass) which changes to a yellowish shade (NiO_6 groups impart a yellow color in glass) when the glass is annealed properly.

Divalent cobalt shows two different types of absorption spectra in aqueous solutions or in the periclase lattice (MgO), where a cobalt ion substitute a magnesium ion surrounded by six oxygen ions. It gives rise to a pink color. The same is the case with low melting borate and phosphate glasses too.

The absorption spectrum of 6-fold coordinated cobalt has a broad band with a maximum in the green region of the spectrum. When the pink borate glass is heated, a considerable change occurs in the light absorption and the pink color changes into a deep blue. The blue color is caused by the cobalt ion in a 4-fold coordination. Generally, the cobalt ion takes a 4-fold coordination at high temperatures and a 6-fold coordination at low temperatures in glass. A glass obtained by quenching the melt of the composition shown in the table 1.5 gives rise to a blue color and the mica crystallized from the melt of the same composition has a pink color. This change is due to the rearrangement of (CoO_4) in the melt into (CoO_6) during crystallization.

Both glass obtained by quenching and mica crystallized from the melts of the composition shown in the table 1.6 or that of ($0.5 K_2SiF_6$, $3 MgO$, $2.5 SiO_2$, $1/6 Co_3O_4$) show a blue color. Different behaviors of the two melts are caused by aluminum ion. In the presence of a sufficient amount of aluminum ion, the cobalt ion changes its coordination from 4-fold to 6-fold. In the presence of an insufficient amount of aluminum ion or in its absence, the 4-fold coordination of cobalt ion remains unchanged during crystallization.

(2) On the Density of Synthetic Mica

Molecular volumes of synthetic and natural micas were calculated from their molecular weights and densities and are shown in Table 4.

Lattice constants of polymorphic micas measured by S. B. Hendricks and M. E. Jefferson[9] and their molecular volumes calculated are shown in Table 5. It

TABLE 4

	Molecular weight	Density	Molecular volume
1. Zn-Mica	437	2.965	147
2. Be-Mica	410	2.770	148
3. Na-Mica	406	2.742	148
4. B-Mica	411	2.743	150
5. Co^p-Mica	427	2.863	149
6. Co^b-Mica	425	2.918	146
7. $Ba_{0.5}$-Mioa	447	2.986	149
8. BaLi-Mica	502	3.338	150
9. SrLi-Mica	456	3.129	145
10. CaLi-Mica	405	2.789	145
11. Ni-Mica	425	2.841	149
12. Mn-Mica	430	2.917	147
13. Fe^{++}-Mica	434	2.904	149
14. $FeAl^{+++}$-Mica	429	2.895	148
15. Fe^{+++}-Mica	444	2.975	149
16. Zn^2-Mica	—	—	—
17. K-phlogopite	425	2.852	149
18. Natural phlogopite	417	2.786	150
19. Natural biotite	443	2.981	149
20. Natural muscovite	415	2.883	144

seems probable that synthetic micas and the natural phlogopite and biotite listed in Table 5 have the single layer monoclinic hemihedral, the two layer monoclinic holohedral (octophillite type), or the six layer monoclinic hemihedral structure. The molecular volume of the natural muscovite corresponds to that of the two layer monoclinic (muscovite type) structure.

TABLE 5

	Lattice constant (Å)			β	Molecular volume
	a	b	c		
1. Single layer monoclinic hemihedral	5.3	9.2	10.2	100°	14_5
2. Two layer monoclinic holohedral, muscovite type	5.2	9.0	20.0	95°30'	14_2
3. Two layer monoclinic holohedral, octophyllite type	5.3	9.2	20.0	95°	14_6
4. Three layer rhombohedral enantiomorphic hemihedral	5.3		30.0		17_0
5. Six layer monoclinic hemihedral	5.3	9.2	60.0	90°	14_8
6. Six layer triclinic holohedral	5.3	5.3	60.0	$\alpha = \beta = 90°$ $\gamma = 120°$	16_0
7. Twenty-four layer triclinic holohedral	5.3	5.3	240.0	$\alpha = \beta = 90°$ $\gamma = 120°$	16_0

The density of mica increases as its molecular weight increases. In other words, the density of a mica crystal depends on the weights of composing atoms.

(3) The Relation of the Size of the Produced Mica Crystal and its Chemical Composition

a. In the case of the substitution of 12-fold coordination potassium

Sizes of K-mica crystals were larger than those of Na-mica crystals. Sizes of mica crystals grow larger as the cations in the 12-fold coordinated position become larger. It was shown in the CaLi-, SrLi-, and BaLi-mica crystals series that sizes of BaLi-mica crystals were the largest, those of SrLi-mica the next, and those of CaLi-mica the smallest. Alkali-earth micas were harder and less cleavable than alkali micas.

b. In the case of the substitution of octahedral magnesium

When larger quantities of magnesium in phlogopite were substituted by other metals, the mica crystals obtained were small. But it was observed in an experiment that when only a small amount of magnesium was substituted by cobalt, crystals grew larger than the pure magnesium mica.

c. In the case of the substitution of tetrahedral aluminum

Crystals of Al-mica were the largest, B-mica the next, and Be-, Zn-, Co-, and Fe-mica smaller.

(4) Conclusions

From the above results, the following facts are obtained.

(1) Principal factors of isomorphous substitution of a cation in mica crystals are (*a*) the size of ion, (*b*) hybrid bond character and (*c*) temperature-dependence of coordination number.

(2) The density of a mica increases as its molecular weight increases. In other words, the density of a mica crystal depends on the weights of composing atoms.

(3) When a small amount of magnesium in fluor-phlogopite $F_2KMg_3(AlSi_3O_{10})$ was substituted by cobalt, crystals grew larger than the other various kinds of synthetic micas.

References

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