Evidence for the Replacement of Silicon by a Divalent Cation: Synthesis of a Novel Zinc Mica, $K_2H_2Zn_5[ZnSi_7O_{20}](OH)_4$

By RICHARD M. BARRER and WERNER SIEBER

(*The Physical Chemistry Laboratories, Chemistry Department, Imperial College, London* SW7 2AY)

Summary The composition and the unit cell dimensions of a novel synthetic mica indicate isomorphous replacement of silicon by zinc.

THE mica group of minerals displays a great variety of isomorphous replacement[1] with relatively minor structural changes. While co-existence of di- and tri-valent cations in the octahedral layer is frequent, substitution of tetrahedral silicon is more restricted, both in terms of elements and proportion of atoms. Aluminium is by far the most frequent element, and the ratio Al:(Al+Si) (tetrahedral) varies between 0[2,3] and *ca.* 0·25:1. A material described as zinc phlogopite was synthesised by Perrota and Garland[4] from a starting gel containing K^+, Al^{3+}, Zn^{2+}, and SiO_2. No analysis of the product was given.

In the present work, a zinc mica has been synthesised in the absence of any trivalent cations. The synthesis could be carried out reproducibly in a platinum-lined autoclave from a mixture of zinc oxide, silica (precipitated, supplied by B.D.H.), and potassium hydroxide solution in the proportions $K_2O:ZnO:SiO_2:H_2O = 0{\cdot}4:1:1{\cdot}8:16$. The mixture was kept at 220 °C for 4 days. The resulting white powder was washed with hot water and dried at 130 °C. Its *X*-ray powder pattern closely resembled that of a synthetic magnesium phlogopite.[3] It was indexed accordingly.[5] The dimensions of the monoclinic unit cell, calculated from 40 reflections, with $Pb(NO_3)_2$ internal standard, are: $a = 0{\cdot}5338$ ($\pm 0{\cdot}0002$), $b = 0{\cdot}9249$ ($\pm 0{\cdot}0003$), $c = 1{\cdot}0350$ ($\pm 0{\cdot}0005$) nm, $\beta = 99°55' \pm 2'$.

Electron micrographs showed platy crystals. The observed density was 3·372 g cm^{-3} (calculated for $Z = 1$, 3·486 g cm^{-3}, assuming the ideal composition $K_2O{\cdot}6ZnO{\cdot}7SiO_2{\cdot}3H_2O$). The results of the chemical analysis are shown in the Table.

TABLE. The composition of the zinc mica

Element	Oxides/ wt. %	Cation numbers [a]	Layer charges
K	8·88	2·01	+2·01
Zn	46·55	5·18[b]	−0·174
		0·918[c]	
Si	39·92	7·08	−1·836
H	4·62	5·47	
(Total)	99·97		

[a] Calculated per 24 oxygens, *cf.* ref. 2. [b] Octahedral zinc. [c] Tetrahedral zinc.

Assigning one zinc atom to the tetrahedral layer appears to be the only plausible way to accommodate the observed components in the mica unit cell. The tetrahedral layer then assumes the same charge as in common micas with Si:Al = 3:1. The octahedral layer of the zinc mica contains more hydroxy groups (in place of oxygens) than usual. This is explicable by the lack of space to accommodate the 6 zinc cations necessary for charge compensation. The only other known example[3] of a mica free from trivalent cations also contains 5 octahedrally co-ordinated (Mg^{2+}) ions per unit cell. Its tetrahedral layer contains only silicon. The *a* and *b* parameters of the present structure are increased by 2% compared with that of ref. 3, in accordance with replacement of 1/8 Si by Zn with a Zn–O distance of 0·195 nm and concurrent shortening of the Si–O(–Zn) bond.[6] The recent *X*-ray study[6] of a framework zincosilicate also provides strong general support for our hypothesis.

We thank W. R. Grace Corp. for financial support.

(*Received, 25th August* 1977; *Com.* 904.)

[1] W. A. Deer, R. A. Howie, and J. Zussman, 'Rock Forming Minerals,' Longmans & Green, London, 1962, vol. 3.
[2] W. S. Wise and H. P. Eugster, *Amer. Mineral.*, 1954, **39**, 1031.
[3] F. Seifert and W. Schreyer, *Amer. Mineral.*, 1965, **50**, 1114.
[4] A. J. Perrota and T. J. Garland, *Amer. Mineral.*, 1975, **60**, 152.
[5] H. S. Yoder and H. P. Eugster, *Geochim. Cosmochim. Acta*, 1954, **6**, 157.
[6] K. F. Hesse, F. Liebau, H. Böhm, P. H. Ribbe, and M. W. Phillips, *Acta Cryst.*, 1977, **B33**, 1333.