THE AMERICAN MINERALOGIST, VOL. 47, SEPTEMBER-OCTOBER, 1962

THE SYNTHESIS AND PROPERTIES OF A FLUORMICA, INTERMEDIATE BETWEEN FLUORTAENIOLITE AND FLUORHECTORITE

John L. Miller and Robert C. Johnson, *Metallurgy Research Laboratory, U. S. Bureau of Mines, Norris, Tennessee.*

Abstract

A monoclinic synthetic fluormineral, which conforms to the hectorite formula but which has the physical characteristics of fluormicas, was prepared. Chemical, physical, optical and *x*-ray data are provided. Chemical analysis data were calculated to an empirical formula of $K_{1.3}Mg_{4.8}Li_{1.25}Si_{7.96}O_{20.03}F_{3.97}$. Physical and optical properties are density, 2.800 g.cm^{-3}; perfect basal cleavage; biaxial (−); α 1.504, β 1.534, γ 1.535, and $2V=2$–$5°$. Unit cell dimensions are a 5.227 Å; b 9.057 Å; c 10.133 Å; β 99°52′; space group $C2/m$.

Introduction

Research on fluor-silicate systems at the Metallurgy Research Laboratory at Norris has produced a number of new, synthetic compounds similar to some minerals. Among the most recently reported are proto-amphibole (Gibbs *et al.* 1960), and fluor-magnesio-richterite. The fluormica reported ($K_{1.3}Mg_{4.8}Li_{1.25}Si_{7.96}O_{20.03}F_{3.97}$) is similar to hectorite ($X_{.66-1.32}Mg_{6-x}Li_xSi_8O_{20}(OH,F)_4$ where X is occupied by potassium. However, the physical characteristics are very much like taeniolite ($K_2Mg_4Li_2Si_8O_{20}(OH,F)_4$.

Synthesis

The new fluormica was synthesized in the course of experiments involving isomorphic substitutions in the general mica formula, $K_{1-2}Y_{4-6}Z_8O_{20}(OH,F)_4$. X is univalent or divalent cations, usually of radii greater than 1 Å. Y refers to intermediate-sized cations (0.6 to 0.9 Å) in six-fold coordination, commonly designated as the octahedral position. Z refers to small or highly charged cations in four-fold coordination with oxygen. Well mixed chemically pure raw materials were placed in graphite crucibles inside fireclay crucibles and fired to 1420° C. for 2 hours. The temperature, decreased rapidly to 1300° C., was then lowered at 10° C. per hour to 1100° C., when the furnace was shut off. Raw materials used were K_2SiF_6, LiF, Li_2CO_3, MgO, and SiO_2. The batch formula used to synthesize the fluormica was $K\ Li\ Mg_4Li_2Si_8O_xF_{4.5}$.

The product of this melt was a well crystallized mass containing two phases, (1) clear platy crystals of about 1 to 2 mm in their greatest dimension and (2) an extremely small flake size water-swelling phase ("lithium fluor-hectorite"). Owing to the presence of the latter the mass was readily broken apart by placing it in water. Agitation with a mechanical stirrer was necessary to effect the complete separation of the two phases; subsequent washing and decanting a number of times removed all traces of the water-swelling phase.

COMPOSITION AND PROPERTIES

Chemical formula and density

Chemical analysis (Table 1, col. 2) was obtained on a sample, which had been thoroughly washed to remove any water-swelling phases and which was examined and selected by means of the binocular microscope to insure purity.

The method of Shell and Craig (1956) was used to calculate the analytical data to the empirical formula $K_{1.3}Mg_{4.8}Li_{1.15}Si_{7.96}O_{20.03}F_{3.97}$.

The total mass units (ZM) of a mole of unit cells were determined from the formula:

$$ZM = \frac{\rho V \times 10^{-24}}{1.6602 \times 10^{-24}}$$

where the measured density, $\rho = 2.800$ g. cm^{-3} at 25° C., and the unit cell volume, $V = 472.61$ Å^3.

By inserting the value of the measured density, ρ, and the unit cell volume, V, into the above equation ZM is determined to be 797.07, the mass in a mole of unit cells. This weight permits the calculation of mass units for each component in the unit cell except oxygen which is assumed sufficient to satisfy the charges of the cations in their respective structural positions. The number of ions per unit cell is as shown in Table 1 and resulted in an empirical formula in good agreement with the one based on 24 ions per unit cell.

The density calculated from the measured cell dimensions and the

TABLE 1. CALCULATION OF THE UNIT CELL CONTENT

	Wt. %	Mass units per mole of unit cells[1]	Molecular weight	No. of ions per unit cell
SiO_2	60.00	478.10	60.06	7.96
MgO	24.29	193.55	40.32	4.80
K_2O	7.72	61.51	94.30	$.65 \times 2 = 1.30$
Li_2O	2.34	18.65	29.88	$.62 \times 2 = 1.24$
F	9.47	75.46	19.00	3.97
H_2O	.20	1.59		
$O = F^-$	−3.99	−31.79		
	100.03	797.07		

---

[1] Results in Col. 1 multiplied by 797.07/100.03. Assuming Z = 1 the empirical formula calculates to $K_{1.30}Mg_{4.80}Li_{1.23}Si_{7.96}O_{20.01}F_{3.97}$.

TABLE 2. OPTICAL PROPERTIES FOR THE NEW SYNTHETIC FLUORMICA, SYNTHETIC FLUORPHLOGOPITE, NATURAL HECTORITE, AND TAENIOLITE

	New synthetic fluormica[1]	Synthetic fluorphlogopite[2]	Natural hectorite[3]	Taeniolite[3] [4]
α	1.504 ± .001	1.519 calc.	1.485(α^1)	1.522 ± .002
β	1.534 ± .001	1.545		1.553
γ	1.535 ± .001	1.547	1.516(γ^1)	1.553
Birefringence	.031	.028	.031	.031
2V	2–5°	about 9°		Approx. uniaxial
Optic sign	(−)	(−)		(−)

[1] M. V. Denny assisted in optical determinations.

[2] Bureau of Standards.

[3] Ross and Hendricks, 1945.

[4] Miser and Stevenson, 1938.

formula derived from chemical analysis was 2.795 g. cm^{-3}. The measured density was obtained by two methods: (1) a Roller Smith microbalance (Berman, 1939) and (2) a Beckman air comparison pycnometer. The measured density by air pycnometer was 2.800 g. cm^{-3}, by microbalance 2.806 g. cm^{-3}.

The accuracy of the air comparison pycnometer was confirmed, using synthetic fluorphlogopite. The density of synthetic fluorphlogopite calculated from cell dimensions was 2.879 ± 0.004 g. cm^{-3} and measured with the Roller Smith microbalance was 2.88_2 g. cm^{-3} (Kohn and Hatch, 1955). The air comparison pycnometer gave 2.87_6 g. cm^{-3} as the density of fluorphlogopite.

Optical properties

Refractive indices were determined by oil immersion techniques. Sodium (D) light was used for all measurements; α was determined from vertically oriented flakes cemented to the inside walls of polyethylene rings mounted on glass slides. The rings served as cups to contain the immersion oils. The optical constants for fluormica, fluorphlogopite, natural hectorite and taeniolite are listed in Table 2.

X-RAY DIFFRACTION DATA

Diffractometer data (Table 3) were obtained by utilizing a Norelco diffractometer. The smear mounting technique was used because the material was platy and required special care to minimize preferred orientation.

The sample was ground with an agate mortar and pestle, and passed

TABLE 3. *X*-RAY POWDER DIFFRACTION DATA

hkl	*I* (meas.)	*d*	*hkl*	*I* (meas.)	*d*
001	86	9.949	131	8	2.468
002	33	4.984	201	33	2.396
020	23	4.512	$22\bar{1}$	5	2.257
110	25	4.479	220	5	2.236
$11\bar{1}$	9	4.329	041	3	2.207
021	5	4.122	$(13\bar{3})$	12	2.143
111	8	3.873	(202)		
$11\bar{2}$	21	3.611	005	30	1.995
003	100	3.325	223	2	1.742
112	32	3.106	134	1	1.728
$11\bar{3}$	24	2.883	$31\bar{1}$	4	1.711
023	11	2.681	$13\bar{5}$	11	1.656
130	22	2.602	311	5	1.619
(200)	24	2.575	152	4	1.590
$(13\bar{1})$			$33\bar{1}$	12	1.509
(113)	9	2.493	136	9	1.350
(004)			117	7	1.304
			008	4	1.248

through a 325 mesh screen onto a BT cut quartz plate (Buerger and Kennedy, 1958) containing a thin layer of petroleum jelly. By placing the BT cut quartz plate with the film of petroleum jelly beneath the 325 mesh screen and brushing the sample through with a camel hair brush, the flakes had less chance of orienting parallel with the plate. The flakes were held in the position in which they landed on the jelly.

Three diffraction charts were made from the sample using nickel filtered CuKα radiation and scanned at $\frac{1}{4}°$ 2θ per minute. Instrument settings were scale factor, 8–16; multiplier, 1.0; time constant, 4; divergence slit, 1°; receiving slit, 0.003″; scatter slit, 1°; chart speed, $\frac{1}{2}°$ per inch. Synthetic spinel ($MgAl_2O_4$) was used as an internal standard.

Bragg reflections were measured by using the proposed method of Donnay and Donnay (1952). This method involves measuring the centers of the peaks at two-thirds height when the α_1 and α_2 spectral components were resolved. When α_1 and α_2 were not readily distinguishable the peaks were measured at half heights as proposed by Smith and Sahama (1954). Averages of the measurements taken from the three charts were converted into Q values from tables compiled by Gibbs and Lewis (1961).

The diffraction data were indexed on the basis of a monoclinic cell with the following dimensions:

$$a = 5.227\ \text{Å}, \quad b = 9.057\ \text{Å}, \quad c = 10.133\ \text{Å}, \quad \beta = 99°52'.$$

The dimensions of the unit cell were checked by single crystal data obtained from precession photographs. A 1M structure type was confirmed by Laue photographs employing the technique of Hendricks and Jefferson (1939). The β angle as measured from precession photographs was 99°53′. Calculated from powder data, using the average of results obtained from 112, $11\bar{2}$ and 131, $13\bar{1}$ peaks, the β angle was 99°52′. The calculated angle between the (100) and the (110) planes was 29°36′.

DISCUSSION

The new synthetic mineral has properties common to both taeniolite and hectorite. Being a 2:1 three-layer-type silicate, it contains a magnesium lithium fluoride layer (brucite type) between two silica tetrahedral layers. The apex oxygen ions of the silica tetrahedra form the octahedral configuration with magnesium, lithium and fluorine of the brucite layer. Fuorine occupies the position filled by hydroxyl in natural hectorite and the micas. The similarity to hectorite lies in the number and configuration of the cations. The general formula for the hectorite end member, $X_{.66-1.32}Mg_{6-x}Li_xSi_8O_{20}(OH,F)_4$, is satisfied by the formula of the new fluormica, $K_{1.30}Mg_{4.80}Li_{1.25}Si_{7.96}O_{20.03}F_{3.97}$. At this point, however, the similarity ends. All physical and optical characteristics are more like fluortaeniolite.

As in both hectorite and taeniolite, the new mineral has no substitution in the tetrahedral layer, which results in the negative charge arising solely from the octahedral layer. Magnesium and lithium in this position provide 11 charges toward the 44 charges needed for neutrality, thereby allowing only one charge for 12-fold coordinated ions. This charge, having to act through a longer distance, is of course weaker than a charge arising from substitution in the silica layers. This condition coupled with the small ionic radius and valence charge of the normal ion occupying this position in natural hectorite (sodium) offers a situation conducive to ion exchange and to expansion in water.

The stability and crystal size is related directly to the presence of potassium in 12-fold coordination. Owing to the size of the potassium cation, much better screening of the electrical charges is afforded. In fact, when a slight change is made in the batch composition ($KLiMg_4Li_2Si_8O_xF_{4.5}$) to conform to the taeniolite batch formula ($K_2Mg_4Li_2Si_8O_{20}F_4$), the result is a non-water-swelling mass of crystals similar in appearance to the new synthetic ompound, but which conforms to the taeniolite formula when chemically analyzed. Only the slight excess of lithium fluoride over that required in the taeniolite formula is necessary to form a water-swelling phase ("lithium fluor-hectorite") and the new synthetic mineral.

The water-swelling phase may be converted into the new phase by cationic exchange of potassium ions for lithium in 12-fold coordination. This is accomplished by dispersing the water-swelling material to form a colloidal suspension and flocculating it with potassium hydroxide. When washed free of potassium hydroxide, the resulting very small crystals are similar in most properties to the new fluormica phase.

ACKNOWLEDGMENTS

Acknowledgment is gratefully made to Dr. William J. Campbell, Supv. Physical Chemist, Bureau of Mines, College Park, Md.; Dr. Gerald V. Gibbs, University of Chicago; Milford L. Skow, Commodity Specialist, Branch of Nonmetallic Minerals, Bureau of Mines, Washington, D. C.; and Haskiel R. Shell, Supv. Inorganic Chemist, Bureau of Mines, Tenn., for critical reading of the manuscript.

REFERENCES

BERMAN, H. (1939), A torsion microbalance for the determinations of specific gravities of minerals. *Am. Mineral.* **24,** 434–440.

BUERGER, M. J. AND G. C. KENNEDY (1958), An improved specimen holder for the focusing type *x*-ray spectrometer. *Am. Mineral.* **43,** 756–757.

DONNAY, G. AND J. D. H. DONNAY (1952), The symmetry change in the high-temperature alkali-feldspar series. *Am. Jour. Sci., Bowen Vol.* Pt **1,** 115–132.

GIBBS, G. V., F. D. BLOSS AND H. R. SHELL (1960), Proto-amphibole, a new polytype. *Am. Mineral.* **45,** 974–989.

——— AND R. M. LEWIS (1961), Quadratic functions for copper radiation −0° to 180° 2θ. *U. S. Bur. Mines, Info. Circ.* **8071,** 1–43.

KOHN, J. A. AND R. A. HATCH (1955), Synthetic mica investigations, VI: *X*-ray and optical data on synthetic fluorphlogopite. *Am. Mineral.* **40,** 10–21.

MISER, H. D. AND R. E. STEVENS (1938), Taeniolite from Magnet Cove, Arkansas. *Am. Mineral.* **23,** 104–110.

ROSS, C. S. AND S. B. HENDRICKS (1945), Minerals of the montmorillonite group. Their origin and relation to soils and clays. *U. S. Geol. Surv. Prof. Paper* **205-B.**

SHELL, H. R. AND R. L. CRAIG (1956), Synthetic mica investigations: VII, Chemical analysis and calculation to unit formula of fluorsilicates. *U. S. Bur. Mines, Rept. Invest.* **5158.**

SMITH, J. V. AND T. G. SAHAMA (1954), Determination of the composition of natural nephelines by an *x*-ray method. *Mineral Mag.* **30,** 439–449.

Manuscript received, March 5, 1962.