Clays and Clay Minerals, Vol. 31, No. 4, 251–260, 1983.

NONCENTRIC LAYER SILICATES: AN OPTICAL SECOND HARMONIC GENERATION, CHEMICAL, AND X-RAY STUDY

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Abstract—Twenty-nine chlorites, seventeen lithium-free micas, and twenty-two lithium-bearing micas from diverse localities have been studied by X-ray diffraction, microprobe, and optical second harmonic generation (SHG) techniques to determine which are noncentric and the cause of acentricity. Manandonite (B-rich chlorite) and cookeite, both crystallizing in the *Ia* form, are acentric. Sudoite-*IIb* gave a questionable SHG signal, possibly indicating acentricity. All other chlorites gave null signals. Bityite, a Li,Be mica similar to margarite, was determined from the positive SHG response to be acentric. It crystallizes in the $2M_1$ form and, by analogy to margarite, is ordered tetrahedrally in subgroup symmetry, *Cc*. Masutomilite-1*M* and "cryophyllite"-1*M* (a zinnwaldite high in Al and Si, but low in Fe) are acentric and most probably crystallize in space group *C*2, thus allowing a noncentric octahedral ordering pattern. Lepidolites showed a diversity in SHG response with only a few being acentric; a lepidolite-1*M* from Mesagrande, California, a lepidolite-3*T* from Windhuk, South West Africa, and a lepidolite-$2M_2$ from Nagatare, Japan, gave positive SHG responses. The Japanese material is complexly intergrown and twinned, and intergrain reflection or refraction may have produced spurious signals.

Most lithium-free micas showed diversity in SHG response and, although most were non-emitters, clintonite from Amity, New York, showed a positive response, but this sample is twinned and shows stacking disorder. A "manganophyllite"-1*M* (manganoan phlogopite) from Langban, Sweden, showed a very weak positive response; however, the presence of Mn alone is not suffcient to produce octahedral cation ordering in noncentric subgroup symmetry. Two manganoan phlogopites from Japan were refined in subgroup symmetry, and the higher order and ideal symmetry of *C*2/*m* was confirmed.

Key Words—Acentricity, Chlorite, Electron microprobe, Lithium, Mica, Second harmonic generation, X-ray diffraction.

INTRODUCTION

Clay mineral structures may be acentric for several reasons. Serpentine minerals lack a center of symmetry because of the very nature of their silicate layers, which consist of one octahedral sheet and one tetrahedral sheet with apical oxygens of a single polarity. Other clay minerals, because of differences in the stacking of successive silicate layers, may be acentric in overall structure even when individual layers are centric. In structures containing more than one cation species occupying sites with similar coordination, an acentric structure may develop when the cations order or order partially. Several such examples have been confirmed by X-ray diffraction analysis (Guggenheim and Bailey, 1977, 1978; Guggenheim, 1981) and by infrared techniques (Farmer and Velde, 1973). Bailey (1975) considered different patterns of atomic ordering, several of which may produce an acentric structure. Because of the large number of variables involved, characterization of the cause or causes of the noncentric nature of the structure is difficult. In fact, it is often very difficult by X-ray diffraction methods to establish if the structure is acentric or not, particularly if the cations are centrosymmetrically arranged and the anions are not.

Franken *et al.* (1961) found that acentric materials emit light at twice the frequency of impinging laser light. Such an effect, known as second harmonic generation (SHG), is produced from the electric field of the laser pulse interacting with the outer electrons of highly polarizable atoms such as oxygen or hydrogen. In contrast to the Giebe and Scheibe (1925) piezoelectric test or techniques that involve crystal morphology, etch figures, or pyroelectricity to determine acentricity, SHG appears to be reliable, rapid, and sensitive (Kurtz and Dougherty, 1979).

Preliminary studies to test the reliability of SHG have only recently been made. Kurtz and Perry (1968) found that the second harmonic signal may be reduced by a decrease in the amount of sample or sample layer thickness, and by absorption effects of the sample. In addition, the intensity may decrease also with decreasing particle size (Kurtz and Perry, 1968; Newnham *et al.*, 1977) and with twinning (Newnham *et al.*, 1977). The signal may either decrease or increase due to preferred orientation (Kurtz and Perry, 1968) and, in several instances, spurious signals (Kurtz and Perry, 1968) can be produced by effects other than the optical harmonics of the sample under study. These effects include damage by grinding, intergrain reflection or refraction,

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https://doi.org/10.1346/CCMN.1983.0310402 Published online by Cambridge University Press

and the presence of noncentric contaminants. Care in sample preparation reduces some causes of spurious signals. Moreover, the other effects producing these signals may be recognized by large bandwidth differences between the second harmonic and a spurious signal, as well as by the signal wave shape or duration.

A limited number of layer silicates have been studied by SHG to determine noncentric structures. Bish *et al.* (1979) and Horsey (1981) showed that all studied samples of zinnwaldite-1M, margarite-2M_1, and ephesite-2M_1 generated signals and that muscovite-2M_1, phlogopite-1M, clintonite-1M, and biotite-1M did not. In addition, Horsey found that a montmorillonite, a penninite, a vermiculite, and two talcs did not produce signals. Guggenheim (unpublished data) found also that six vermiculites and two interstratified (10-Å and 14-Å phases) samples did not produce signals. Of four lepidolites studied by Horsey, a lepidolite-1M from Tanakamiyama, Japan, produced a signal and was later shown by Guggenheim (1981) to have a noncentric octahedral ordering pattern. Guggenheim (1981) concluded that not all lepidolite-1M micas are similarly ordered; thus it seems reasonable to assume that other layer silicate species may show variations as well. The present paper reports SHG, chemical, and X-ray diffraction data on a large number of layer silicates in an attempt to identify acentric materials.

EXPERIMENTAL

A SHG instrument similar to that described by Bish *et al.* (1979) was used, except that higher bandwidth electronics and a cooled photomultiplier tube housing were added for noise reduction. To avoid a system that was too sensitive and which would detect higher order effects not related to acentricity (quadrupole interactions, etc.), the system was calibrated with standardized powdered quartz and $BaTiO_3$ ceramic samples (Dougherty and Kurtz, 1976).

Cleavage flakes were optically examined under polarized light at 125× to eliminate possible spurious signals due to foreign material. All flakes containing inclusions and other impurities were rejected. Most samples were examined in single crystal form either as large flakes or groups of flakes with the laser pulses directed perpendicular to the (001) plane to minimize the effects of grinding, reflection, and refraction. Because of this sample orientation, the test being only sensitive to asymmetries perpendicular to the laser beam, and the lack of a defined zero level in SHG analysis, the test cannot be used to prove a centric structure.

The integrated intensity of the second harmonic signal, the number of signal spikes, and the correlation to the fundamental were used to determine acentricity. Emphasis was placed on the latter two because most signals were weak. At least six laser firings (each firing containing 20 to 200 lasing pulses) were made for each sample. The results fall into three categories: null or no signal for all firings, a positive signal for all firings, and a questionable signal. A questionable signal represents inconsistent results (a sequence of null and positive firings with one or two signal spikes of low intensity). To minimize the possibility of laser damage, the test was started at a minimum power level and the average intensity was increased at successive firings. This procedure allowed a judgment of the degree of laser-damage-induced SHG signal. If when returning to low power the signal was significantly increased, it was assumed that damage had occurred. It is difficult to assign a value to the minimum signal, but the level is probably two to three orders of magnitude below that given by powdered quartz.

Compositional data were obtained from a three-spectrometer MAC-5 automated electron microprobe using the data-reduction procedure of Bence and Albee (1968) and incorporating the alpha factors of Albee and Ray (1970). Analyses of Ni and Zn were obtained using a modified ZAF procedure based on the "Magic" program of J. W. Colby of Bell Telephone Laboratories, Allentown, Pennsylvania. Analyses of F, Na, Mg, and Al were made with a RAP crystal and flow proportional counter spectrometer, Si, K, Ca, Ti, Rb, and Cs with a PET crystal, and Cr, Mn, Fe, Ni, Zn, and Ba with a LiF crystal. The LiF crystal was used with sealed proportional counter spectrometers. Each analysis represents an average of at least three individual analyses and, generally, many more. The electron beam was broadened and the sample current kept as low as possible to minimize sample damage. Standards used were: hornblende, Kakanui, New Zealand (Smithsonian sample #NMNH-143965), for Si, Al, Fe, Mg, Ca, Na, Ti; benitoite, San Benito County, California (NMNH-86539), for Ba; microcline, locality unknown (NMNH-143966), for K; albite, Amelia County, Virginia, for Na; lepidolite, Radkovice, Czechoslovakia, for F, Rb, Cs; hypersthene, Johnstown, Colorado, meteorite (NMNH-746) for Cr; fayalite, Rockport, Maine (NMNH-85276), for Mn; and zinc and nickel metal.

All samples were examined by Debye-Scherrer or Gandolfi X-ray powder methods and, for those samples giving positive SHG signals, by the single crystal Buerger precession X-ray method. Specimens for powder analysis were prepared by abrading a cleavage plate with an iron file to prevent structural damage by grinding that might reduce the X-ray intensities of reflections. For samples producing null or questionable SHG signals, polytype information given in the tables most likely represents the dominant stacking sequence in the specimen inasmuch as only a small sample portion was examined. The single crystal analyses of all other samples allowed an assessment of relative crystallinity and stacking regularity, in addition to a confirmation of polytype as determined from the powder films. Because the 1M and 3T polytypes are indistinguishable from

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powder patterns, the single crystal analysis proved useful to differentiate the two. Samples showing noncentric contaminating phases in the X-ray analysis were removed from further consideration.

Because bityite (Li,Be-rich mica) and manandonite (B-rich chlorite) have not been extensively studied, the type specimens (bityite: Harvard #87680; manandonite: NMNH #140978) were also analyzed by ion microprobe by Ian M. Steele of the University of Chicago following the procedures outlined in Steele *et al.* (1981). Because a lithium layer-silicate standard was unavailable, the analysis was determined by reference to count-rate ratios of each unknown to a spodumene assumed to be stoichiometric. Boron and beryllium analyses were determined using published data (Meyer, 1978; Gittens *et al.*, 1972) for relative secondary ion yields of each element relative to aluminum. Count rates for B, Be, and Al were measured and approximate B/Al and Be/Al ratios derived and combined with the electron microprobe data to produce ratios for bityite (Si:Al:Li:B:Be:Ca = 5.18:7.41:1.70:0.61:3.41:2.37) and for manandonite (5.28:8.87:3.19:2.22:0.02:0.01). These ratios yield structural formulae of $Ca_{0.9}Li_{0.65}Al_{2.1}(Al_{0.7}Be_{1.3}Si_{1.97}O_{10}(OH)_2$ and $Li_{1.55}Al_{4.0}(B_{1.08}Si_{2.57}Al_{0.35})O_{10}(OH)_8$, respectively. Error estimates are believed to be better than a factor of two (Steele *et al.*, 1981). Data on composition, polytypes and SHG are given in Table 1 for the micas, Table 2 for the lithium-rich micas, and Table 3 for the chlorites. Because lithium cannot be analyzed by electron microprobe, all of those samples given in Table 2 may not have appreciable amounts of lithium, particularly those of the $2M_1$ polytype which may be closer to lithian muscovite in structure (Levinson, 1953).

DISCUSSION

Micas

Lithium,beryllium micas from four localities were examined (Table 2, samples 1–4). Compositional data for the type locality sample of bityite, as determined by ion and electron microprobes, confirm previous wet chemical and spectroscopic analyses for bityite as described by Fleischer (1950). A small, highly twinned (see Strunz, 1956) sample from Mt. Bity gave a positive SHG signal, as did untwinned samples from the Mops and No Beer Pegmatites, which contained less lithium and beryllium. The sample from the Namaherere Mine gave a questionable signal, but this sample is intermixed with substantial amounts of muscovite which would attenuate the signal. Consequently, it is likely that each of these samples is acentric.

The Li,Be micas form a compositional series from the trioctahedral end member of bityite to the dioctahedral end member, margarite, with vacancy and aluminum replacement for lithium and beryllium, respectively. Margarite-$2M_1$ has been shown by Guggenheim and Bailey (1977) to have a nearly ordered silicon and aluminum tetrahedral pattern that violates the center of symmetry of the ideal space group $C2/c$. The Li,Be micas, also crystallizing as $2M_1$, may form a similar pattern with the ordering of Al, Be, and Si tetrahedra. Farmer and Velde (1973) suggested such a pattern from infrared spectra, and Lin and Guggenheim (1983) confirmed this pattern by a single crystal X-ray refinement of the Mops sample.

The other lithium-rich micas gave a wide range of results. The Mn analogue of zinnwaldite, masotumilite (sample 21, Table 2), produced a relatively strong SHG response. Although the ideal space group is $C2/m$ for the $1M$ polytype of zinnwaldite, Guggenheim and Bailey (1978) showed that aluminum prefers an octahedral site that is related by a pseudomirror plane to a larger, lithium- and iron-rich octahedral site. Masotumilite, by analogy, probably has similar octahedral ordering and therefore also maintains a reduced symmetry to space group $C2$.

A variety of zinnwaldite (sample 15, Table 2), known as "cryophyllite" in the older literature (Foster, 1960), is high in aluminum and silicon, and contains less iron. Although this specimen gave a relatively strong positive SHG signal, the iron-rich biotite (sample 17, Table 1) from the same locality did not. However, the latter sample is very dark and may be opaque to the laser pulse.

The lepidolite-$1M$ (sample 13, Table 2) from Mesagrande, California, has regular stacking and produced a second harmonic signal equal approximately in response to that of zinnwaldite. The chemical analysis implies few possible cation-ordering effects, except Al for Si tetrahedrally, or Li (and vacancy) for aluminum octahedrally. By analogy with the recent refinement of lepidolite-$1M$ (Guggenheim, 1981) from Tanakamiyama, Japan, in which Al is related by a pseudomirror plane to a larger octahedral site, this mica may have a similar (and acentric) octahedral ordering pattern.

The lepidolite-$2M_2$ (sample 18, Table 2) from Nagatare, Japan, is the only sample of that polytype that produced a positive SHG signal. Optical microscope and X-ray diffraction precession examinations indicate complex twinning and intergrowths making further single crystal X-ray study difficult. The partial chemical analysis presented in Table 2 is comparable to that of the Mesagrande lepidolite, and similar arguments can be made that octahedral cation ordering may be responsible for noncentrosymmetry in this structure. Twinning, therefore, may be related to the unique ordering scheme. However, it is unclear whether twinning (causing reflection and/or refraction at twin boundaries) may produce the positive SHG response; these conclusions are therefore, tentative.

The positive (although very weak) SHG response from the manganoan phlogopite ("manganophyllite") from Langban, Sweden (sample 11, Table 1) and a

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https://doi.org/10.1346/CCMN.1983.0310402 Published online by Cambridge University Press

Table 1. Second harmonic generation data, X-ray electron microprobe (partial analyses) data, and structural formulae of micas.

	1	2	3	4	5	6[3]	7	8	9	10	11	12	13	14	15	16	17
Polytype	$2M_1$	$1M+2M_1$	$2M_1$	$2M_1$	$2M_1$	$1M_d$	$1M$	$1M_d$	$1M_d$	$1M$	$1M$	$1M_d+2M_1$	$2M_1$	$1M$	$1M_d$	$1M$	$1M$
SHG Result[1]	0	?	0	0	?	0	0	?	+	?	+	0	0	0	0	0	0
SiO_2	46.83	54.74	45.86	46.83	45.57	31.62	17.56	18.02	19.07	42.33	41.16	39.11	37.59	43.20	36.09	40.33	38.19
Al_2O_3	28.72	20.76	33.14	32.92	35.76	12.19	39.09	37.56	40.09	8.70	14.26	19.35	15.30	12.09	14.53	11.37	12.63
FeO[2]	2.81	0.70	3.06	1.21	0.54	5.60	3.39	3.88	2.83	3.54	2.58	11.31	7.61	0.08	22.11	18.85	36.53
MgO	1.95	6.30	0.77	1.34	0.74	1.43	20.00	19.62	20.33	22.46	25.23	14.04	21.24	25.61	11.36	15.47	0.06
MnO	0.68	0.92	0.50		0.04	14.96	0.06		0.04	7.57	1.18	0.18	0.09		0.48	0.41	0.60
TiO_2	0.98	0.35		1.00	1.26	0.26			0.33		0.37	0.06	3.83		1.50	2.20	1.46
Cr_2O_3				0.49	0.65	0.06					0.14	0.07	0.13				
ZnO						21.54						0.08					
NiO												0.11					
K_2O	11.15	11.86	11.89	10.22	9.11	8.15		0.01	0.02	10.12	11.05	9.61	9.94	10.23	9.53	8.96	8.71
CaO					0.02		14.41	14.04	14.05	0.04		0.04	0.03			0.06	
Na_2O				0.30	1.11	0.77					0.38		0.88			0.12	
BaO				0.36	2.80	0.72					0.54		0.64			0.30	
F														2.48	1.37	2.38	0.38
Total	93.11	95.59	94.21	94.67	97.60	97.31	94.51	93.13	96.74	94.76	96.89	93.97	97.38	93.69	96.97	100.45	98.56
O = F														1.04	0.58	1.00	0.16
Total														92.65	96.39	99.45	98.40
Formulae based on 22 positive charges																	
Si	3.24	3.65	3.11	3.14	3.01	2.80	1.27	1.25	1.33	3.12	2.89	2.88	2.69	3.12	2.80	2.97	3.05
Al(IV)	0.76	0.35	0.89	0.86	0.99	1.20	2.73	2.75	2.67	0.76[4]	1.11	1.12	1.29[4]	0.88	1.20	0.99	0.95
Al(VI)	1.59	1.28	1.76	1.74	1.79	0.06	0.60	0.32	1.64		0.07	0.56		0.15	0.12		0.24
Fe^{2+}	0.16	0.04	0.17	0.07	0.03	0.41	0.20	0.23	0.17	0.22	0.15	0.70	0.46		1.43	1.16	2.44
Mg	0.20	0.63	0.08	0.13	0.07	0.19	2.15	2.03	2.12	2.46	2.63	1.54	2.27	2.75	1.31	1.70	0.01
Mn	0.04	0.05	0.03			0.91				0.47	0.07	0.01	0.01		0.03	0.03	0.04
Ti	0.05	0.02		0.05	0.06	0.02			0.02		0.02		0.21		0.09	0.12	0.09
Cr				0.03	0.03												
Zn						1.41											
K	0.98	1.01	1.03	0.87	0.77	0.92				0.95	0.99	0.90	0.91	0.94	0.94	0.84	0.89
Ca							1.11	1.04	1.05							0.00	
Na				0.04	0.14	0.13					0.05		0.12			0.02	
Ba				0.01	0.07	0.03					0.01		0.02			0.01	
Σoct	2.04	2.02	2.04	2.02	1.98	3.00	2.95	2.58	2.95		2.94	2.81		2.90	2.98	3.01	2.82

[1] For second harmonic generation (SHG) signal: 0 = null or no signal, + = positive signal, ? = inconsistent results (see text).
[2] All data assumed FeO.
[3] Inhomogeneous in chemistry.
[4] Tetrahedral deficiency probably made up by Fe^{3+}.

Comments, locality and donor information by column

(1) "alurgite," Ultevis, Lappland, Sweden: SWB; (2) "alurgite," St. Marcel, Italy: AMNH; (3) "alurgite", Minas Gerais, Brazil: SWB; (4) "fuchsite," Tamative, Madagascar: SWB; (5) "fuchsite," near Leydodorp, Transvaal, South Africa; (6) hendricksite, Franklin, New Jersey; (7) clintonite, Lago della Vacca, Adamello Mountains, Italy; (8) clintonite,

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Table 1. Continued.

Crestmore, California; (9) twinned, may be 3*T*, clintonite, Amity, Orange County, New York: SWB; (10) "manganophyllite," Pajsberg, Sweden: ANMH-13456; (11) "manganophyllite," Langban, Sweden: AMNH-26752; (12) sample size marginal, locality unknown: SWB; (13) Loolmurwak Crater, Tanzania; (14) "eastonite," Easton, Pennsylvania: NMNH-C3760; (15) sample very dark, Philadelphia, Pennsylvania: GC-462.B7; (16) sample very dark, Silver Crater Mine, Bancroft, Ontario: SWB; (17) sample very dark, Cape Ann, Massachusetts: FM-14462. Donor abbreviations: SWB = S. W. Bailey Collection; AMNH = American Museum of Natural History, New York; NMNH = Smithsonian Institute, Washington; GC = Genth Collection, Pennsylvania State University; FM = Field Museum of Chicago, Illinois.

Table 2. Second harmonic generation data, X-ray data, and partial chemical analyses of lithium micas.

	1[3]	2[4]	3[5]	4[6]	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21[8]	22
Polytype	$2M_1$	$2M_1$	$2M_1$	$2M_1$	1*M*	3*T*	$2M_1$	1*M* + $2M_2$	$2M_1$	$2M_1$	$2M_1$	1*M*	1*M*	$2M_2$	1*M*	$2M_2$	$2M_2$	$2M_2$	1*M*	$2M_1$	1*M*	$2M_1$
SHG signal[1]	+	?	+	+	0	+	?	0	0	0	0	0	+	0	+	0	?	+	0	0	+	+
SiO_2	33.1	32	31.26		53.50	50.44	46.51	51.27	51.65	45.21	43.78	51.33	52.71	47.49	52.35	49.74	52.10	51.41	51.09	49.93	48.64	47.13
Al_2O_3	37.0	42	44.37		21.04	20.65	31.02	21.77	28.67[7]	35.53	35.89	23.28	23.82	28.74	16.58	22.97	26.87[7]	26.68	22.75	28.91	21.87	33.53
FeO[2]					0.09	2.50	2.60	0.45	0.01	1.10	0.73	0.02		0.05	8.51	0.06	0.09		0.08	0.62	1.31	2.44
MgO	0.1					0.20				0.03	0.02	0.23			0.08	0.03						0.005
MnO					0.50	2.38	0.65	0.54	0.55		0.02	0.15	0.57	0.44	0.31	1.02	0.50	0.34	0.43	1.51	7.39	0.06
Cs_2O									0.97				2.63				2.12	1.87			0.83	
K_2O	0.03	0.5	0.008		10.70	11.39	10.81	10.49	11.12	10.66	10.82	11.20	11.37	11.50	10.19	9.16	11.28	11.21	10.55	11.31	9.96	8.93
Na_2O	0.1	0.8	0.19					0.05	0.17	0.30	0.31	0.12	0.11		0.12	0.54		0.32			0.20	0.41
Rb_2O					0.97	0.75	1.04	0.92	0.81	0.05		0.88	0.59	0.76	0.69	3.49	1.38	0.68	1.33	0.42	1.74	
CaO	14.5	14	13.64																			
F					7.22	5.43	6.11	6.76	4.81	5.95	6.23	5.95	6.75	6.70	7.43	4.88	6.43	4.54	5.77	4.92	6.35	
Total	99.95	97.85	100.94		94.02	93.74	98.74	92.25	98.76	98.83	97.80	93.16	98.55	95.68	96.26	91.89	100.77	97.05	92.00	97.62	98.60	92.51
O = F					3.04	2.28	2.57	2.84	2.03	2.50	2.62	2.50	2.84	2.82	3.13	2.05	2.70	1.91	2.43	2.07	2.67	
Total	99.95	97.85	100.94		90.98	91.46	96.17	89.41	96.73	96.33	95.18	90.66	95.71	92.86	93.13	89.84	98.07	95.14	89.57	95.55	95.93	92.51

[1] For SHG signal: 0 = null or no signal, + = positive signal, ? = inconsistent results (see text).
[2] All data assumed FeO.
[3] Includes BeO: 7.2; Li_2O: 1.8; Fe_2O_3: 0.02; H_2O: 6.1; data from Gallagher and Hawkes, 1966 (wet chemical data).
[4] Includes BeO: 2.5; Li_2O: 0.05; H_2O: 6; data from Gallagher and Hawkes, 1966 (wet chemical data).
[5] Includes BeO: 4.1; Li_2O: 2.1; Fe_2O_3: 0.17; H_2O: 5.1; see Lin and Guggenheim, 1983 (probe and wet chemical data).
[6] See text for chemistry.
[7] Inhomogeneous with respect to Al.
[8] Includes ZnO: 0.31.

Comments, locality and donor information by column

(1) "beryllium margarite," No Beer Pegmatite, Bikita district, Zimbabwe: G#1848; (2) "beryllium margarite," Namherere Mine, Ankole, Uganda: G#1825; (3) "beryllium margarite," Mops Pegmatite, Salisbury District, Zimbabwe: G#1847; (4) specimen from A. Lacroix, bityite, Mt. Bity Madagascar, Harvard #87680; (5) 1*M* twinned polysynthetically to simulate 3*T* precession photos, see Sadanaga and Takéuchi (1961), Cocanarup, Western Australia: BM1919, 52; (6) Windhuk, Southwest Africa: UWA4; (7) Ledoc Mine, Wakefield Township, Quebec: UW390; (8) Usakos, Southwest Africa; BM1927.912; (9) sample size marginal, Spencer #11 Claim, Farm Daawib East: #6, Karibab District, South Africa: UWEG51-302; (10) Etta Mine, Keystone, South Dakota: UWEG5-10-3; (11) Alabascha, Urals: SWB; (12) Pala, California: Harvard #89733; (13) Mesagrande, San Diego County, California; FM#M803b; (14) Hebron, Maine: E. Lyons (collector), SWB; (15) "cryophyllite," Cape Ann, Massachusetts: FM#14453; (16) Sajany, Siberia, U.S.S.R.; (17) different cleavages produced differing SHG results from a consistently null signal to a very weak positive one, some 1*M* possibly present, Auburn, Maine, SWB. Another Auburn specimen, with significant stacking disorder, produces a positive response; (18) Nagatare, Fukuoka, Japan: Kyushu University #207-1; (19) sample size marginal, Stewart Mine, Pala, California: SWB; (20) sample size marginal, Anderson #1 Mine, East Hampton, Connecticut: UWEG49-11-6; (21) masutomilite, Murzinka, Urals: BM38456; (22) "irvingite," Stettin, Wisconsin. Donor abbreviations: G = M. J. Gallagher; BM = British Museum; UWEG = University of Wisconsin Economic Geology Collection; UW = University of Wisconsin Museum Collection; SWB = S. W. Bailey Collection; FM = Field Museum of Chicago, Illinois.

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Table 3. Second harmonic generation data, X-ray, electron microprobe (partial analyses) data, and structural formulae of the chlorites.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Polytype	*IIb*	*IIb*	*IIb*	*Ib*(90°)	*IIb*	*IIb*	*IIb*	*IIb*	*IIb*	*IIb*	*IIb*	*IIb*	*IIb*	*IIb*	*IIb*
SHG Signal[1]	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
SiO_2	31.38	28.81	30.87	25.16	27.32	42.82	25.24	29.86	25.83	24.68	32.28	33.23	31.09	31.13	30.76
Al_2O_3	14.69	24.07	23.30	18.81	20.92	13.89	21.43	20.86	26.19	23.06	15.32	13.07	16.41	17.06	18.51
FeO[2]	4.61	7.09	0.02	34.54	12.66	7.43	29.30	12.02	9.78	20.73	3.71	8.97	4.62	4.82	3.64
MgO	29.54	25.95	28.40	9.38	23.08	23.14	12.60	24.38	26.16	17.61	32.78	30.26	28.14	28.15	28.43
MnO	0.02	0.06		0.76	0.14	0.07	0.48	0.36	0.23	0.10		0.07	0.01	0.02	0.01
Total	80.24	85.98	82.60	88.65	84.13	87.84	89.05	87.47	88.19	86.19	84.09	85.59	80.28	81.60	81.36
							Formulae based on 28 positive charges								
Si	3.22	2.78	2.97	2.77	2.80	3.97	2.68	2.92	2.49	2.58	3.15	3.27	3.18	3.15	3.08
Al(IV)	.78	1.22	1.03	1.23	1.20	0.03	1.32	1.08	1.51	1.42	0.85	0.73	0.82	0.85	.92
Al(VI)	.99	1.52	1.62	1.21	1.33	1.49	1.36	1.32	1.46	1.42	0.91	0.79	1.16	1.18	1.27
Fe^{2+}	.40	.57		3.18	1.08	0.58	2.60	0.98	0.78	1.81	0.30	0.74	0.39	0.41	0.31
Mg	4.51	3.74	4.08	1.53	3.52	3.20	1.99	3.55	3.76	2.75	4.76	4.44	4.29	4.24	4.25
Mn				0.07	0.01	0.01	0.04	0.03	0.02	0.01		0.01			
Σoct.	5.90	5.83	5.70	5.99	5.94	5.28	5.99	5.88	6.02	5.99	5.97	5.98	5.84	5.83	5.83

	16	17	18	19	20	21	22	23[3]	24	25	26	27	28[4]	29[5]
Polytype	*IIb*	*IIb*	*IIb*	*IIb*	*IIb*	*IIb*	*IIb*	*Ia*	*IIb*	*Ia*	*IIb*	*Ia*	*Ia*	*Ia*
SHG Signal[1]	0	0	0	0	0	0	0	0	?	0	0	+	+	+
SiO_2	27.26	29.15	34.09	35.77	33.89	34.66	31.37	28.2	32.85	35.45	27.27	37.28	34.7	
Al_2O_3	23.07	25.03	14.38	12.42	15.30	14.86	14.60	11.2	35.42	48.12	22.61	43.90	48.4	
FeO[2]	15.57	0.46	4.72	4.24	4.82	0.49	5.56	20.2	3.44	0.12	8.08	0.29	0.1	
MgO	23.36	31.66	30.32	35.44	33.04	35.44	31.02	12.8	13.02	0.22	28.04	0.01		
MnO	0.32	0.04	0.03	0.08	0.09	0.88	0.06		0.26		0.09			
TiO_2								1.0						
Ni								14.6						
Total	89.56	86.33	83.53	87.93	87.14	86.32	82.61	88.0	84.99	83.91	86.09			
							Formulae based on 28 positive charges							
Si	2.66	2.72	3.34	3.34	3.20	3.24	3.15	2.93	3.05	3.17	2.67			
Al(IV)	1.34	1.28	0.66	0.66	0.80	0.76	0.85	1.07	0.95	0.83	1.33			
Al(VI)	1.31	1.47	1.00	0.71	0.90	0.88	0.88	0.30	2.93	4.25	1.28			
Fe^{2+}	1.27	0.04	0.39	0.33	0.38	0.04	0.47	1.75[3]	0.27	0.01	0.66			
Mg	3.40	4.40	4.43	4.93	4.65	4.94	4.64	1.98	1.80	0.03	4.09			
Mn	0.03			0.01	0.01	0.07	0.01		0.02		0.01			
Ti								0.08						
Ni								1.22						
Σoct.	6.01	5.91	5.82	5.98	5.94	5.93	6.00	5.33	5.02	4.29	6.04			

[1] For SHG signal: 0 = null or no signal, + = positive signal, ? = inconsistent results (see text).
[2] All data assumed FeO.

Table 3. Continued.

[3] Data from Bailey and Riley, 1977; read as $Fe^{3+} = 1.08$, $Fe^{2+} = 0.67$.
[4] Data from Miser and Milton, 1964 by X-ray fluorescence and microspectrography: read FeO as Fe_2O_3. Additional values are CaO = 0.2; $Na_2O = 0.01$; $Li_2O = 2.2$ by microspectrography and 2.7 by wet analysis; $H_2O = 13.8$ by wet analysis.
[5] See text for chemistry.

Comments, locality and donor information by column

(1) Texas, Pennsylvania: PS517; (2) North Carolina: UW19229; (3) Prilep: SWB; (4) Arakawa Mine, Japan: SWB; (5) Flagstaff Hill area, El Dorado County, near Sacramento, California: Post; (6) inhomogeneous with respect to Si, possibly impure, Lebanon County, Pennsylvania: UW19404; (7) sample size marginal, Burke Mountains, Vermont: SWB; (8) Flagstaff Hill area, El Dorado County, near Sacramento, California: Post; (9) Achmatovsk, Urals, AMNH; (10) Salida, California: UW21456; (11) West Chester, Pennsylvania: NMNH-R4513; (12) Ogushi Hizen, Japan: NMNH-87144; (13) West Chester, Pennsylvania: UW21020; (14) Tilly Foster Mine, New York: NMNH-R4512; (15) Birmingham, Pennsylvania: UW19405; (16) Lowell, Orleans County, Vermont: AMNH-18424; (17) "sheridanite," Miles City, Montana: NMNH-94515; (18) Flagstaff Hill area, El Dorado County, near Sacramento, California: Post; (19) Viesch, Switzerland: UW19284; (20) Flagstaff Hill area, El Dorado County, near Sacramento, California: Post; (21) Langban, Varmland, Sweden: AMNH-28982; (22) see Steinfink, 1958, Mochako District, Kenya: Harvard #97703; (23) Nimite, Woodline Well, near South Windarra, Western Australia: SWB; (24) Sudoite with pyrophyllite impurity, sample size marginal, Stavelot Massif, near Ottre, Belgium, SWB; (25) donbassite, Novaya Zemlya, U.S.S.R.: SWB; (26) Macon County, North Carolina: UW19938; (27) Li not analyzed, cookeite, Londonberry, Western Australia, SWB; (28) Li not analyzed, cookeite, Jeffrey Quarry, Little Rock, Arkansas: CMS; (29) manandonite, Antandronkomby, Madagascar, NMNH-140978. Donor abbreviations: PS = Pennsylvania State Collection; UW = University of Wisconsin Museum Collection; SWB = S. W. Bailey Collection; AMNH = American Museum of Natural History, New York; NMNH = Smithsonian Institute, Washington; CMS = source clay The Clay Mineral Society.

questionable signal from a similar mica from Pajsberg, Sweden (sample 10, Table 1) suggest that manganoan phlogopites of 1*M* polytype have a tendency for cation ordering in noncentric subgroups of *C*2/*m*. (X-ray diffraction precession photographs indicate regular stacking.) To test this hypothesis, single crystal X-ray data for samples 1 and 5 (both manganobarium phlogopites) from Kato *et al.* (1979) were re-examined. The refinement follows the procedure summarized by Guggenheim (1981) and involves all possible cation-ordering schemes in *C*2 symmetry. (Space group symmetry *Cm* was not checked, because tetrahedral cation ordering is less likely.) For both crystals, the ideal space group, *C*2/*m*, accounted for the data better than the noncentric space group, in accord with Kato *et al.* (1979). These results indicate that manganese in the mica structure does not, by itself, promote octahedral cation ordering and that different manganoan micas may have different ordering patterns. A similar situation exists for lepidolite (see Guggenheim, 1981) in which composition alone does not promote cation ordering (ordering has been attributed to parameters of crystallization other than compositional effects). However, for manganoan phlogopite, compositional effects still should be considered as a possible variable.

The yellow mica from Stettin, Wisconsin (sample 22, Table 2), appears slightly weathered. Although this sample produced a (very weak) positive SHG response, it seems unlikely from the microprobe data that the crystalline material has the capacity for significant octahedral cation ordering. Precession photos indicate regular stacking; however, unlike any of the other studied micas that gave a signal, precession photographs also indicated significant mosaic spread. Mosaic spread is an indication of crystalline discontinuity and is analogous to the effect of line broadening observed in X-ray powder diffraction films when damage to the sample is induced by grinding. The positive SHG signal in this case is probably due to sample damage caused by the weathering. On the other hand, there is no positive evidence for this interpretation, and Al and Si ordering in the tetrahedral sites is possible in either *Cc* symmetry or in domains that would space average to *C*2/*c* symmetry when studied by diffraction methods. Furthermore, mosaic spread is apparently common in the chlorites, but few chlorites show a positive SHG response.

Chlorites

The ion microprobe data for manandonite, although not of high precision, confirm the chemistry indicated by Frank-Kamenetskii (1960) as a dioctahedral (with trioctahedral interlayer) Li,Al chlorite with substantial tetrahedral boron. Of the twenty-nine chlorite specimens examined, only the lithium-rich varieties appear to have acentric structures. These lithium-rich chlorites, cookeite and manandonite, are distinguished by

https://doi.org/10.1346/CCMN.1983.0310402 Published online by Cambridge University Press

forming di,trioctahedral structures and crystallizing in the relatively rare *Ia* polytype. Single crystal precession photos of manandonite show extensive streaking (with some maxima) of the $k \neq 3n$ type reflection for $0kl$ nets, and although it may be argued that an approach to semirandom stacking could produce an overall structure that is noncentric, many of the chlorites in Table 3 also show such streaking, but do not give positive SHG results (in accord with expected insensitivity to asymmetries parallel to the laser beam direction as discussed above).

Lister (1966) showed that cookeite usually adopts one of two layer stacking sequences based on the *Ia* polytype. One of these two forms can be well crystallized and has been reported by Bailey (1975) to occur in the ideal space group of *Cc* with possible octahedral and tetrahedral ordering. The second form is the more common type and is poorly crystalline; its space group has not been determined. Although additional work is required to determine if manandonite falls into the former or latter variety, the refinement of the manandonite structure to determine tetrahedral ordering of B, Al, and Si is not possible. Unfortunately, reflections of the type $k \neq 3n$ are required in single crystal X-ray analysis to characterize tetrahedral site occupancies for the chlorites.

We note also that two chlorites examined here, which do not show a positive SHG response, have been refined successfully in noncentric space groups. These are donbassite (sample 25, Table 3), Novaya Zemlya, U.S.S.R. (Aleksandrova *et al.*, 1972), and "corundophyllite" (sample 22, Table 3), Mochako District, Kenya (Steinfink, 1958). The present results do not necessarily indicate that these refinements are in error, as a lack of signal is not definitive for centrosymmetry.

ACKNOWLEDGMENTS

We thank S. W. Bailey of the University of Wisconsin-Madison, J. L. Post of California State University at Sacramento, M. J. Gallagher of the Institute of Geological Sciences, Edinburgh, D. Atkin of the Institute of Geological Sciences, London, and P. Bender for samples. In addition, we gratefully acknowledge receiving samples from the American Museum of Natural History-New York, the British Museum, the Field Museum of Chicago, the Harvard Museum, the Smithsonian Institute, the University of Wisconsin-Madison Economic Geology Collection, and the University of Wisconsin-Madison Mineral Museum. S. Guggenheim sincerely appreciates the hospitality and use of the Pennsylvania State University laboratories under the direction of R. E. Newnham. Thanks are due to T. Kato of Yamaguchi University for use of his X-ray diffraction data and to S. W. Bailey for reviewing the manuscript. The ion probe analyses were made by Ian Steele of the University of Chicago and supported by NSF grant EAR 77-27100 to J. V. Smith. Portions of this work were supported by a grant from the University of Illinois-Chicago Research Board and by the National Science Foundation under grant EAR 80-18222.

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(Received 1 November 1982; accepted 26 January 1983)

Резюме—Двадцать девять образцов хлоритов, семнадцать образцов обезлитиевой слюды и двадцать два образца слюды, содержащей литий, из различных районов исследовались при помощи рентгеновской порощковой дифракции, рентгеновского микроанализатора и оптической генерации второй гармоники (ГВГ), для определения, какие образцы не имеют центров обратного равенства и причины этого отсутствия. Манандонит (B-обогащенный хлорит) и кукеит, оба кристаллизирующиеся в виле *Ia*, не имеют центров инверсии. Судоит—*IIb* дает сомнительный сигнал ГВГ, возможно в результате отсутствия центра инверсии. Все другие хлориты давали нулевые сигналы. Битиит, Li,Be-слюда подобная маргариту, была определена как не имеющяя центра инверсии по положительном сигнале ГВГ. Этот минерал кристаллизируется в виде $2M_1$ и, по аналогии с маргаритом, упорядочен тетраэдрическо в подгруппе симметрии *Cc*. Мазутомилит—1*M* и "криофиллит"—1*M* (цинвальдит обогащенный Al и Si, но убогий в Fe) не имеют центров инверсии и бодее вероятно кристаллизируются в пространственной гпуппе *C*2, таким образом делая возможным октаэдрическое упорядочение. Лепидолиты показали различные сигналы ГВГ и только некоторые не имели центров инверсии; лепидолит—1*M* из Мезагранде в Калифорнии, лепидолит—3*T* из Линдгук в Южно-Западной Африке и лепидолит—$2M_2$ из Нагатаре в Японии дали положительные сигналы ГВГ. Японский материал являеся сложно прорастанным и спаренным; межзернистое отражение или рефракция могли быть причиной появления ложных сигналов.

Большинство обезлитиевых слюд показало различные сигналы ГВГ и, хотя болышинство являлось неизлучающими, клинтонит из Амиты в Нью Иорке давал положительный сигнал, но этот образец был спаренный и показывал неупорядоченность. "Манганофил"—1*M* (Mn-флогопит) из Лангбан в Швеции давал очень слабый положительный сигнал; однако, присутствие одного только Mn недостаточно, чтобы образовать октаэдрическое упорядочение катионов в подгруппе симметрии без центра инверсии. Два Mn-флогопиты из Японии были усовершенствованы в подгруппе симметрии и лучший порядок и идеальная симметрия *C*2/*m* были подтверждены. [E.G.]

Resümee—29 Chlorite, 17 Li-freie Glimmer, und 22 Li-hältige Glimmer von verschiedenen Fundpunkten wurden mittels Röntgendiffraktion, Mikrosonde und Optical Second Harmonic Generation (SHG) untersucht, um festzustellen, welche nichtzentrisch sind, und was die Ursache für die Azentrizität ist. Manandonit (B-reicher Chlorit) und Kookeit, die beide in der *Ia*-Form kristallisieren, sind azentrisch. Sudoit-*IIb* gab ein nicht eindeutiges SHG-Signal, das möglicherweise eine Nichtzentrizität andeutet. Alle anderen Chlorite gaben keine Signale. Bityit, ein Li-Be-Glimmer, ähnlich Margarit, wurde anhand der positiven SHG-Signale als azentrisch eingestuft. Er kristallisiert in der $2M_1$-Form und ist in Analogie zu Margarit tetraedrisch in der Untergruppe *Cc* geordnet. Masutomilit-1*M* und "Kryophyllit"-1*M* (ein Zinnwaldit mit viel Al und Si aber wenig Fe) sind azentrisch und kristallisieren höchstwahrscheinlich in der Raumgruppe *C*2, wodurch eine nichtzentrische oktaedrische Anordnung möglich ist. Lepidolith zeigt uneinheitliche SHG-Signale, von denen nur einige azentrisch sind; ein Lepidolith-1*M* von Mesagrande, Kalifornien, ein Lepidolith-3*T* von Windhuk, Südwestafrika, und ein Lepidolith-$2M_2$ von Nagatare, Japan, gaben positive SHG-Signale. Das japanische Material ist sehr vielfältig verwachsen und verzwillingt, und Korngrenzen-Reflexion oder -Refraktion könnten die Ursache für die schwachen Signale sein.

Die meisten Li-freien Glimmer zeigen uneinheitliche SHG-Signale und—obwohl die meisten nicht emittieren—zeigte Clintonit von Amity, New York, ein positives Signal. Diese Probe war jedoch verzwillingt und hatte Stapelungsfehler. Ein Manganophyllit-1*M* (Mangan-haltiger Phlogopit) von Langban, Schweden, zeigte ein sehr schwaches positives Signal. Die Anwesenheit von Mn allein reicht jedoch nicht aus, um eine oktaedrische Kationenanordnung in einer nichtzentrischen Untergruppe zu bewirken. Die Strukturen von zwei Mangan-haltigen Phlogopiten aus Japan wurden verfeinert, und die höhere Ordnung und die ideale Symmetrie von *C*2/*m* wurde bestätigt. [U.W.]

https://doi.org/10.1346/CCMN.1983.0310402 Published online by Cambridge University Press

Résumé—On a étudié vignt-neuf chlorites, dix-sept micas sans lithium, et vignt-deux micas contenant du lithium provenant de diverses localités par des techniques de diffraction des rayons-X, microprobes, et optiques de seconde génération harmonique (SHG) pour déterminer lesquelles sont non-centriques, et la cause de l'acentricité. La monandonite (chlorite riche en B) et la cookeite, se cristallisant tous deux en la forme *Ia,* sont acentriques. La sudoite-*IIb* a produit un signal SHG douteux, indiquant possiblement de l'acentricité. Toutes les autres chlorites ont produit des signaux nuls. On a determiné à partir d'une reponse SHG positive que la bityite, un mica Li,Be semblable à la margarite, était acentrique. Elle se cristallise en la forme $2M_1$ et, par analogie avec la margarite, est ordonnée tetraèdralement en symmetrie de sous-groupe *Cc*. La masutomilite-1*M* et la "cryophyllite"-1*M* (une zinnwaldite riche en Al et Si mais pauvre en Fe) sont acentriques et se cristallisent probablement dans le groupe d'espace *C*2, permettant ainsi un cliché d'ordonnement octaèdral non-centrique. Les lepidolites ont montré une diversité dans les réponses SHG avec seulement quelques unes étant acentriques; une lépidolite-1*M* de Mesagrande, Californie, une lépidolite-3*T* de Windhuk, Afrique du Sud-ouest, et une lépidolite-$2M_2$ de Nagatare, Japon, ont produit des réponses SHG positives. Une croissance intersticielle et un jumelage complexes sont présents dans le matériau japonais et la réflection et la réfraction intergrains pourraient avoir produit de faux signaux.

Le plupart des micas sans lithium ont montré une diver sité de réponses SHG, et malgré que la plupart étaient non-émetteurs, une clintonite d'Amity, New York, a produit une réponse positive, mais cet échantillon est jumellé et montre un empillement desordonné. Une "manganophyllite-1*M*" (phlogopite manganoanne) de Langbau, Suède, a produit une réponse positive très faible; la seule présence de Mn n'est cependant pas suffisante pour produire un ordonnement de cations octaèdral en symmétrie non-centrique de sous-groupe. Deux phlogopites manganoannes du Japon étaient rafinées en symmétrie de sous-groupe, et l'ordre plus élevé et la symmétrie idéale de *C*2/*m* ont été confirmés. [D.J.]

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