RELATION OF MECHANICAL PROPERTIES TO THE STRUCTURE OF IONIC SOLIDS

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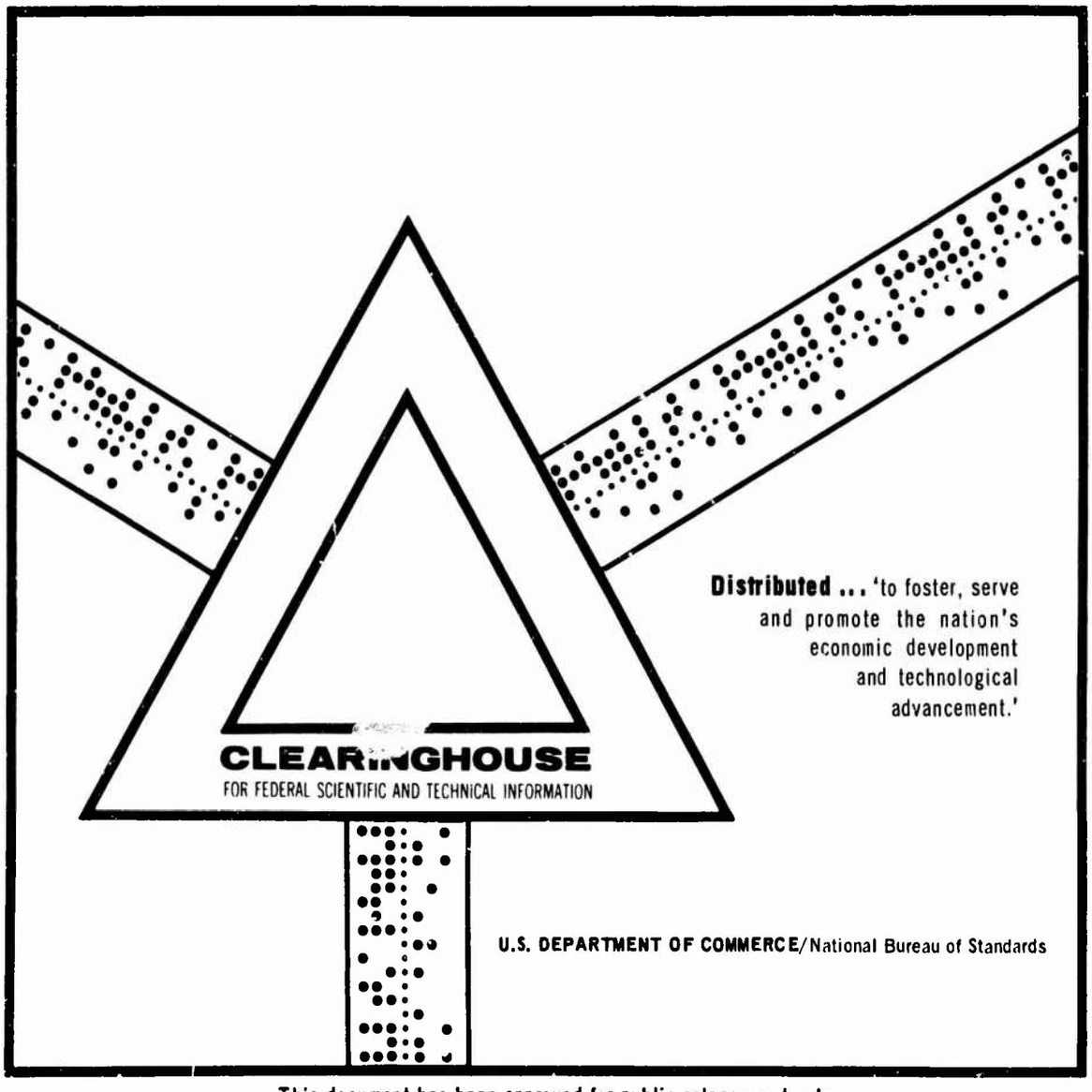
20 August 1969



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RELATION OF MECHANICAL PROPERTIES TO THE STRUCTURE OF IONIC SOLIDS

Final Report

by

K. Vedam
R. E. Newnham
J. W. McCauley
J. L. Caslavsky

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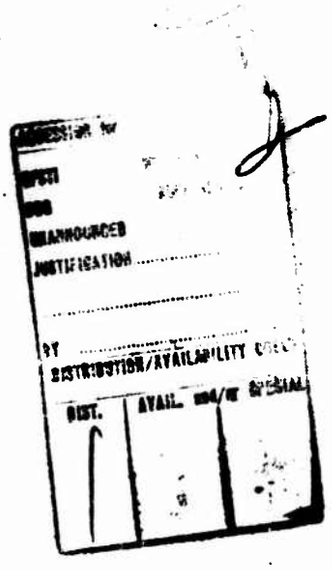
Materials Research Laboratory
The Pennsylvania State University
University Park, Pennsylvania

Contract No. DA-19-0660 AMC-325(X)

ARMY MATERIALS AND MECHANICS RESEARCH CENTER
WATERTOWN, MASSACHUSETTS 02172



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ABSTRACT

The crystal structures of $KMg_3AlSi_3O_{10}F_2$ and $BaLiMg_2AlSi_3O_{10}F_2$ were refined by least squares analysis of x-ray diffraction intensities. It is shown that the hardness, thermal stability and chemical resistance of various micas are related primarily to the interlayer structure and the amount of ditrigonal distortion. Making use of Lang's x-ray topographic technique, partial dislocations with the Burgers vectors 1/2 [1$\bar{1}$0], 1/3 [010] and 1/6 [3$\bar{1}$0] have been photographed in muscovite mica. This is the first time partial dislocations have been observed in mica. The various mechanical properties and the origin of the coarse corrugations which are often observed in muscovite have been explained in terms of the above partial dislocations.

1. Introduction

The primary objective of this project is to strive towards the development of an ideal ductile ceramic by (i) carrying out a detailed investigation of the various fundamental mechanical properties of the layer structure silicates, namely the micas, (ii) concurrently carrying out the detailed crystal structure analyses of these micas in order to understand the origin of the many desirable mechanical properties of mica, and finally (iii) tailor-making new micas based on the above studies. As envisaged in the original proposal this project was to have been operative for a period of five years, of which the last two years would have been devoted mainly to the synthesis of new micas. As mentioned in the earlier reports, one phase of the structural aspect of the project has already been completed, in that two of the four crystal structural studies originally envisaged, namely those of K and Ba-Li fluorophlogopites have been completed; the analyses of the remaining two structures are being carried out at the Army Materials and Mechanics Research Center. Studies on the mechanical properties aspect of this project have also been extremely fruitful, namely, unequivocal evidence for the presence of partial dislocations in mica have been obtained and with this it has been possible to explain the origin of some of the unique mechanical properties of mica. This, being the final report, summarizes the results obtained both in the structural and mechanical properties aspects of the project. For obvious reasons, research work on the third aspect, i.e. to tailor-make new micas based on the results of the other two, was to have started in the ensuing (fourth) year, and hence no detailed account of this aspect is included in this report. However, since both Drs. J. W. McCauley and J. L. Caslavsky have joined the AMMRC, further work along these lines are expected to be continued at the AMMRC itself. Before the actual description of the results obtained, we list below the particulars of the various papers presented, published or submitted for publication, etc., and the degrees granted - which are the direct result of this project.

2. Degrees Granted

1. J. W. McCauley: Ph.D. in Solid State Science, The Pennsylvania State University, 1968. Title of Thesis: Crystal Structures of the Micas $KMg_3AlSi_3O_{10}F_2$ and $BaLiMg_2AlSi_3O_{10}F_2$.
2. J. L. Caslavsky: Ph.D. in Geochemistry and Mineralogy, The Pennsylvania State University, 1969. Title of Thesis: Dislocation Structures and the Mechanical Properties of Mica.

3. Papers Presented

a. CASLAVSKY, J., and VEDAM, K. Dislocations and Mechanical Properties of Muscovite, Acta Cryst. 25A Part S3 Supplement, p. 13 (1969). Presented at the International Congress of Crystallography, 15 August 1969 at Stonybrook, L. I., N. Y.

b. MC CAULEY, J. W., NEWNHAM, R. E., VEDAM, K. and GIBBS, G. V. Crystal Structure Analysis of Synthetic Fluorophlogopite, Geological Society of America Special Paper 115, New Orleans, La., November 1967.

c. MC CAULEY, J. W. and NEWNHAM, R. E. New Aspects in the Predition of Mica Structures, Geological Society of America Meeting, Mexico City, Mexico, November 1968.

d. MC CAULEY, J. W. and NEWNHAM, R. E. Crystal Structure Refinement of the Synthetic Mica 1M-$BaLiMg_2AlSi_3O_{10}F_2$, American Crystallographic Association Meeting, Seattle, Washington, March 1969.

e. VEDAM, K., NEWNHAM, R. E., MC CAULEY, J. W., CASLAVSKY, J. and ROY, R. Relation of Mechanical Properties to the Structure of Micas, Symposium on Structural Ceramic and Design, Chicago, Illinois, March 12-13, 1968.

f. VEDAM, K., CASLAVSKY, J., VAND, V. and ROY, R. Relation of the Mechanical Properties to the Structure of Ionic Solids, Symposium on Structural Ceramics, Chicago, Illinois, March 28-30, 1967.

4. Papers Published or Under Publication

1. CASLAVSKY, J. and VEDAM, K. Examination of Imperfect Muscovite Crystals by X-ray Diffraction Methods, J. Appl. Phys. 41 (January 1970 issue).

2. CASLAVSKY, J. and VEDAM, K. The Study of Dislocations in Muscovite Mica by X-ray Transmission Topography, submitted to Phil. Mag.

3. CASLAVSKY, J. and VEDAM, K. True and Apparent Mechanical Properties of Muscovite, submitted to Am. Mineral.

4. CASLAVSKY, J. and VEDAM, K. Epitaxial Growth of Ice Crystals on the Muscovite Cleavage Plane and Their Relation to Dislocation Structure (to be published).

5. MC CAULEY, J. W., NEWNHAM, R. E., VEDAM, K. and GIBBS, G. V. Geological Society of America Special Paper 115, 1967.

6. VEDAM, K., NEWNHAM, R. E., MC CAULEY, J. W., CASLAVSKY, J. and ROY, R. In "Structural Ceramics and Design," S. J. Acquaviva and S. A. Bortz, eds., Gordon and Breach, 1970.

7. YOON, H. S. and NEWNHAM, R. E. Elastic Properties of Fluorapatite, Am. Mineral. V. 54, 1969, p. 1193.

5. Mechanical Properties of Mica

A literature search revealed almost total absence of reliable data on the fundamental mechanical properties of the very important layer silicate minerals - the micas. The only data reported in the literature are those of Alexandrov and Ryzhova [1] who have determined the elastic constants of muscovite, biotite and phlogopite by the ultrasonic pulse echo method. They assumed these crystals to be of hexagonal symmetry for these measurements and further, all their studies were carried out on one specimen which was kept under compression during the measurements.

Considering the unique mechanical behavior of mica and its immense industrial importance, this lack of data on its mechanical properties is rather surprising. Some of the major reasons for this are (i) the total inapplicability of the usual techniques of sample preparation, fabrication and measurement, (ii) the low crystallographic symmetry of the mica, and (iii) nonavailability of large, perfect crystals, etc. This study reports the measurements on mechanical properties of muscovite on well characterized specimens, and further brings out the various features necessary for properly characterizing the mica crystals for such measurements.

Extensive measurements on the Young's modulus of muscovite mica in its basal plane have been carried out with the help of a bending device designed and constructed specially for materials like mica. The results of these measurements revealed that these crystals could be grouped into two categories: (i) crystals which are elastically pseudo-anisotropic in the basal plane, and (ii) crystals which are almost elastically isotropic in the basal plane.

The crystals belonging to the first category were found to exhibit anomalous x-ray contrast in the Berg-Barrett topographs as sharply contrasting striations or stripes resembling dislocation lines. A detailed analysis of the contrast behavior of the striations showed that they are formed not by dislocations but by the corrugation of the basal planes of muscovite single crystals. The directions of the corrugation were found to be along [100], [110] and [1$\bar{1}$0] crystallographic directions. It was found that the width of these striations, as well as the spacings between them, are in the range of 0.001 cm and 0.05 cm, and that there is no regularity even in the same specimen.

No correlation between the Young's modulus of the specimen and the density or the number of striations could be detected. However, all corrugated muscovite samples exhibited systematically lower values of Young's moduli when compared with values obtained from the non-corrugated crystals. The minimum value of Young's modulus of corrugated samples was found when the axis of deformation in bending was parallel with the direction of corrugation.

The value of the Young's modulus in the basal planes of the crystals belonging to category (ii) was found to be $(1.59 \pm 0.05) \times 10^{12}$ dyne cm^{-2}. This value is in fairly good agreement with the value 1.65×10^{12} dyne cm^{-2} computed from the elastic constants data of Alexandrov and Ryzhova [1].

Studies reported on the dislocation kinetics in mica are also very few. Amelinckx and Delavignette [2] did not find any evidence for partial or incomplete dislocations in mica even though they were able to detect them in every other layer structure examined, i.e. talc, chlorite, MoS_2, etc. However, it must be noted that Amelinckx's studies on mica were not exhaustive since his samples dehydroxylated under the influence of the electron beam in the electron microscope. Since the mechanical properties of mica can be considerably influenced by the presence of partial dislocations if present, this aspect has been considered in some detail in this study.

It follows from consideration of the self-energy of a dislocation line and Frank's rule that only partial dislocations should be favored in mica structures. On the other hand, the high energy of stacking fault associated with partial dislocation argues against the existence of partial dislocations.

At the present time, the behavior of dislocations and their possible reactions are very well understood only for simple highly symmetric lattices for which they are applicable. Hence the problem of partial dislocations in mica cannot be resolved by analogy with other structures. Hence it was necessary to resort to the experimental proof of the existence of partial dislocations in mica.

The existence of perfect or total dislocations in muscovite in the basal plane has been reported by Demny [3]. Hence the partial dislocation, if any, must also be situated on the same plane. Owing to the location of these dislocations and the natural shape of muscovite crystals, the x-ray transmission topography was used as a suitable technique for delineating them. Assuming that the corrugation may be formed by anomaly of the slip, the corrugated muscovite crystals were selected as the most probable source of partial dislocations. First topographs from corrugated muscovite crystals disclosed a complicated structure and very high density of dislocations. However, it was noticed that the topographs obtained in 130 reflections showed a noticeable decrease of dislocation density. This indicated the presence of dislocations with 1/6 $[3\bar{1}0]$ partial Burgers vectors. Further, it was noticed that the density of dislocations decreases as one proceeds toward the central portions of large crystals exhibiting corrugated structure. Unequivocal proof of the existence of partial dislocations in muscovite was obtained on a crystal (#107793, courtesy of the Smithsonian Institution, Washington, D. C.), which was 24 mm thick. The final dimension of the sample after fabrication was 20 x 20 x 0.18 mm. The sample was free of cleavage steps and was found

to be optically uniform. From the x-ray transmission topographs taken in six diagnostically important reflections, dislocations with the Burgers vectors [100], 1/6 [3$\bar{1}$0] and 1/3 [010] were found. Further, according to their contrast behavior it was concluded that all the dislocations present in muscovite were decorated with impurities. This indicates that the dislocations were formed during the period of crystal growth and formation.

Owing to the symmetry of muscovite, the distinction of dislocations with Burgers vectors 1/6 [310] and 1/6 [3$\bar{1}$0] was not possible by the Lang method if both of them were not present in the same crystal. The existence of dislocations with both these Burgers vectors directions was inferred from epicaxial growth of ice crystals on the cleavage plane of muscovite single crystals.

It may be noticed that the directions of the Burgers vector of the partial dislocations are orthogonal to the direction of the corrugations in the muscovite crystals. This provides a possible clue to the origin of the corrugation observed in muscovite crystals as possibly due to anomalies in slip which occurred during the early history of the crystal formation. The slip in muscovite can proceed only along partial vector directions and advance one length of the partial Burgers vector. However, if the slip is forced by any external forces to continue in its initial slip direction, then coarse structural deformations will occur and result in the corrugation of basal planes.

6. Crystal Structural Studies on Mica

The crystal structure of synthetic 1M-fluorophlogopite (C2/m; $\underline{a}$ = 5.308(2), $\underline{b}$ = 9.183(3), $\underline{c}$ = 10.139(1)Å; β = 100.07(2)°; Z = 2; $K_{0.98}Na_{0.04}Mg_{2.97}Al_{1.02}Si_{2.98}O_{9.90}F_{1.94}(OH)_{0.16}$ has been refined to a weighted R factor of 6.1% by anisotropic least-squares methods employing counter diffractometer data. Intensities of 1546 x-ray reflections were measured and combined by symmetry into 520 non-equivalent, non-zero observed structure amplitudes, and weighted by the range estimate method. Various tests (N(Z) tests, difference Fourier maps, and refinement in non-centric space groups) failed to reveal Al-Si ordering in the tetrahedral sheets. The small tetrahedral rotation angle 5.88° accounts for the small difference between the mean inner (3.006Å) and outer (3.273Å) K-O distances. In fluorophlogopite the interlayer thickness of 3.357Å is much less than that of hydroxyphlogopite (3.61Å). The tetrahedral sheet of fluorophlogopite is quite regular and exhibits a mean T-O distance of 1.642(2)Å; the mean basal O-O distance is 2.667Å and the basal-apical O-O distance is 2.694Å. The following mean interatomic distances were measured in the octahedral sheet: Mg-O = 2.078Å, Mg-F = 2.034Å, O-F(unshared) = 3.065Å, O-O(unshared) = 3.060Å, O-O(shared) = 2.827Å, O-F(shared) = 2.733Å, and F-F(shared) = 2.635Å. The thickness of the octahedral sheet (2.124Å) and the mean Mg-O(F) distance (2.063Å) yield an octahedral flattening angle of 59.02°. All the ions except O_3 (apical), F and Mg_2 show significant anisotropic apparent vibration. Al-Si disorder and the rigidity of the cationic coordination sphere seem to control the magnitude and anisotropy of the oxygen ellipsoids.

The crystal structure of 1M-$BaLiMg_2AlSi_3O_{10}F_2$ (C2/m; $\underline{a}$ = 5.2858(2), $\underline{b}$ = 9.1575(6), $\underline{c}$ = 10.0375(5)Å; β = 100.124(4)°; Z = 2) has been refined in like manner to an R factor of 7.1% utilizing 479 non-equivalent, non-zero observed structure amplitudes. Least-squares refinements in C2 and Cm, and others in C2/m with varying ratios of Li to Mg in the M_1 and M_2 sites failed to reveal significant long range cation ordering in the octahedral and tetrahedral sheets. Electron density and difference maps confirmed these results. This mica is similar to α-$BaAl_2Si_2O_8$ - a 2:0 layer silicate. Barium mica exhibits an even lower rotation (4.73°) than fluorophlogopite, necessitating a proportional decrease in the difference between the outer (3.192Å) and inner (2.975Å) interlayer cation-oxygen distances. Further, the substitution of Ba for K contracts the interlayer separation and slightly distorts the tetrahedral sheet; the basal O-O distances (2.652Å) are shortened with respect to the basal-apical O-O distances (2.715Å). The T-O (apical distance (1.605Å) is also significantly shortened with respect to the T-O (basal) distances (1.657Å) in response to residual negative and positive charges on the apical and basal oxygens respectively. The octahedral sheet is more regular than in fluorophlogopite due to weaker octahedral cation-cation repulsion and also possibly to increased attraction between Ba and F. The mean M-O(F) distance (2.066Å) and the octahedral sheet thickness (2.154Å) yield an octahedral flattening angle of 58.58°, slightly less than fluorophlogopite. All the atoms except Ba and O_1 (basal) are statistically isotropic. The addition of octahedral sheet disorder to tetrahedral sheet disorder results in an increase in the apparent vibration of the oxygen ions.

The orientation of the anisotropic thermal ellipsoids of Ba and K coincide exactly. This may be related to the displacements of both of these atoms from the geometric center of the coordination sphere.

A critical examination of all refined mica structures revealed a linear relationship between α and the difference (Δ) between the outer and inner interlayer cation-oxygen distances. The equation for the best fit line through the points for 13 micas

$$\Delta = K\alpha - 0.02 \qquad (1)$$

$$K = 0.047 \text{ Å/degrees}$$

may be used to estimate the interlayer structure of micas if an accurate value for α can be obtained. From an analysis of the rotation of ideal tetrahedra, an equation was mathematically derived which relates Δ to α, the basal O-O distance, and the interlayer thickness. Using 2.64Å for the O-O distance and an interlayer thickness of 3.00Å, a curve was obtained that showed excellent agreement with the observed data.

An explanation was then sought for the ditrigonal tetrahedral sheet distortion. The tetrahedral-octahedral sheet misfit and the interlayer cation are the two most likely sources for the alternate rotation of

tetrahedra. An unprejudiced misfit parameter was obtained by calculating the ideal dimensions of the octahedral (b_o) and tetrahedral (b_t) sheets from bond lengths. Field strength (charge/ionic radius) was used to estimate the effect of the interlayer cation on the mica structure. A multiple regression equation was derived from the data of ten well refined micas

$$\alpha = 218.0\ (b_t/b_o) - 1.5\ (\text{field strength}) - 221.5 \qquad (2)$$

which demonstrated that the primary control of the tetrahedral sheet distortion is the tetrahedral-octahedral sheet misfit (b_t/b_o).

Equations (1) and (2) can be used to predict α and an approximate interlayer structure from chemical composition data alone. It was demonstrated that equation (2) predicts a much more accurate value of α (2.90) for fluor-polylithionite) than does the Donnay, et al. [4] nomogran (12°); the observed α is 3.0°. Shortening of basal O-O edges leads to erroneous predictions of α using the Radoslovich [5] formula, especially for α less than about 6.5°.

It is well known that trioctahedral micas commonly have stacking faults, whereas dioctahedral micas do not. Fluorophlogopite fits this pattern, but barium mica is a trioctahedral mica free of stacking disorder. The large basal plane corrugation (∿0.2Å) of dioctahedral micas with respect to trioctahedral (∿0.01Å) micas has often been postulated as the reason for the lack of stacking faults in dioctahedral micas. The observation, that hexagonal $CaAl_2Si_2O_8$ (a 2:0 layer structure) exhibits stacking faults whereas α-$BaAl_2Si_2O_2$ does not, led to the suggestion that the large divalent barium ion restricts rotation of successive layers in much the same manner as basal plane corrugation in dioctahedral micas.

Finally, the relation of properties to crystal structure was examined for fluorophlogopite, barium mica and three other micas. It was demonstrated that the origin of the properties can be related primarily to the interlayer structure and the amount of ditrigonal distortion.

7. References

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2. AMELINCKX, S. and DELAVIGNETTE, P. Electron-Microscopic Observations of Dislocations in Silicate Layer Structures. Mechanical Properties Engineering Ceramics, Proceedings Conference, Raleigh, North Carolina, 1960, pp. 105-123.

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