LBL-14291 c.2
Preprint

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

RECEIVED
LAWRENCE
BERKELEY LABORATORY

JUN 18 1982

LIBRARY AND
DOCUMENTS SECTION

Materials & Molecular Research Division

Submitted to Philosophical Magazine

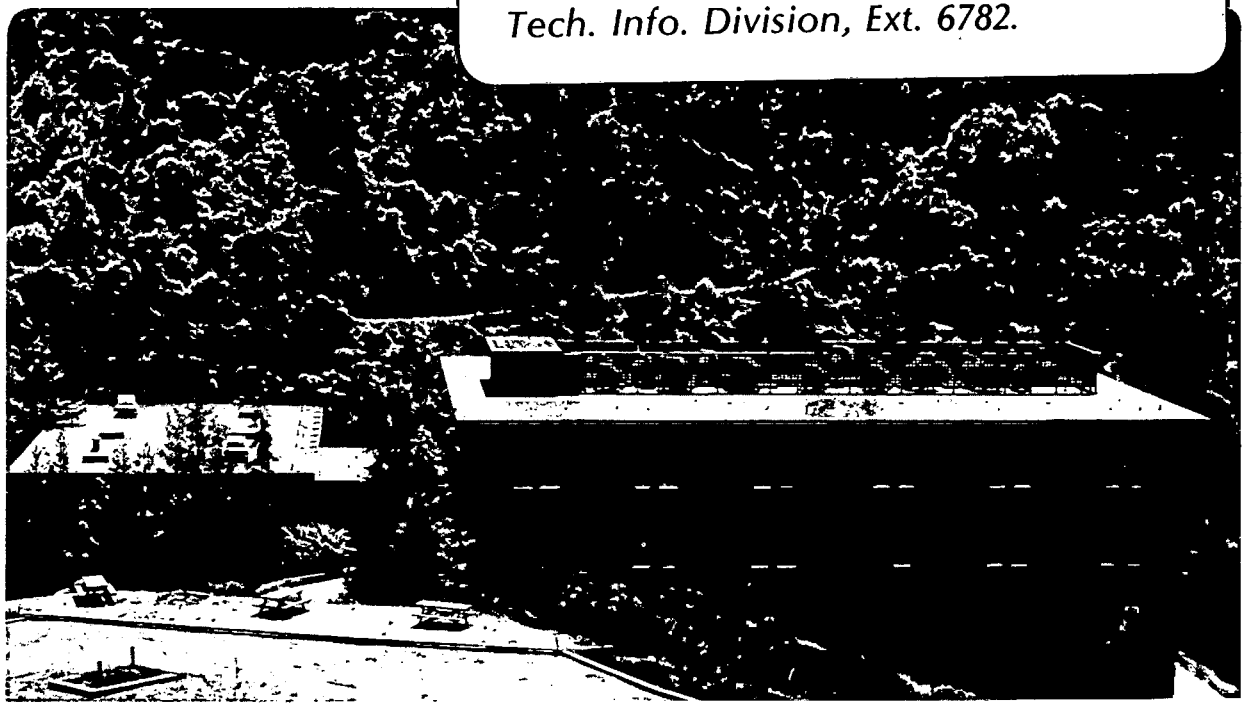
STRUCTURE AND NON-STOICHIOMETRY OF CALCIUM ALUMINATES

Herbert Schmid and Lutgard C. De Jonghe

April 1982

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 6782.



LBL-14291 c.2

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBL-14291

Structure and Non-Stoichiometry of Calcium Aluminates*

Herbert Schmid[†] and Lutgard C. De Jonghe[†‡]

[†]Materials and Molecular Research Division
Lawrence Berkeley Laboratory
Berkeley, California 94720

and

[‡]Department of Materials Science and Mineral Engineering
University of California
Berkeley, California 94720

*This work was supported by the Division of Materials Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract No. DE-AC03-76SF00098.

Structure and Non-Stoicheiometry of Calcium Aluminates*

Herbert Schmid[†] and Lutgard C. De Jonghe[†‡]

[†]Materials and Molecular Research Division
Lawrence Berkeley Laboratory
Berkeley, California 94720

and

[‡]Department of Materials Science and Mineral Engineering
University of California
Berkeley, California 94720

ABSTRACT

Lattice imaging of reaction-sintered ceramic compounds in the CaO-Al_2O_3 (C-A) system showed 00.1 syntactic intergrowths in the matrix $CaO.6Al_2O_3$ (CA_6**) phase. The structure of these intergrowths could be interpreted with the concepts used to describe various magnetoplumbite phases (Braun 1957). The observed formation of syntactic phases reveals that calcium aluminates can accommodate C/A non-stoichiometry in a relatively wide range by altering the stacking sequence of 3 sub-unit cell 00.1 slabs.

*This work was supported by the Division of Materials Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract No. DE-AC03-76F00048.

**C = CaO; A = Al_2O_3

§1 INTRODUCTION

Calcium aluminates have an important role in the chemistry of ceramics, since they form the basis of many refractories and high temperature cements. The system was first investigated by Shepherd, et al. (1909) who reported C_3A*, C_5A_3, CA and C_3A_5 to be stable phases. The C_3A_5 was analysed by x-ray diffraction and found to be CA_2 by Lagerquist, et al (1938). These authors also reported a new, high alumina compound with a C_3A_{16} composition. Adelsköld (1937) examined magnetoplumbite and related isomorphous structures and proposed CA_6 as a stable phase. This was confirmed by Filonenko and Lavrov (1949) and later by Gentile and Foster (1963). The most recent phase diagram for the $CaO-Al_2O_3$ pseudo-binary system now includes C_3A, CA, CA_2 and CA_6 (Nurse, et al 1956). Allibert et al (1981) found CA_6 to be the most stable phase; some uncertainty still exists about another phase, $C_{12}A_7$, since it may contain some water (Nurse et al 1965a; Cockayne and Lent 1975).

Ceramic alloys were prepared for the present study by reacting dense, polycrystalline alumina with a liquid of approximately eutectic composition (C/A≈1 by weight), at 1530°C for about 4 hours. The reaction zone was then examined by transmission electron microscopy and by x-ray microanalysis in an analytic transmission electron microscope. The foils showed planar defects in the CA_6 phase similar to those found in sodium-beta and -beta" aluminas (Sato and Hirotsu 1976; De Jonghe 1977a,b). Similarities should be expected since both sodium-beta alumi-

---

*C = CaO; A = Al_2O_3

nas and CA_6 have a structure that is closely related to that of magnetoplumbite (Adelskold 1938); sodium-beta alumina and CA_6 have identical 00.1 spinel slabs consisting of $(Al_{11}O_{16})^+$ separated by a layer containing Na^+ or Ca^{++}. This interspinel layer has the composition $(NaO)^-$ in sodium-beta alumina and $(CaAlO_3)^-$ in CA_6. The similarities of these structures with magnetoplumbite suggests that the observed planar defects might be syntactic intergrowth whose structure could be described by the formalism developed by Braun (1957).

§2 RESULTS AND DISCUSSIONS

A low magnification image of a faulted CA_6 grain is shown in Fig. 1. The faults are on (00.1) planes and are shown in a 00.1 lattice image in Fig. 2. Figure 2a is imaged with a <01.0> type zone axis parallel to the beam, so that only $\ell=2n$ (n integer) reflections appear in the diffraction pattern, as expected for the magnetoplumbite structure. With a <11.0> zone axis parallel to the beam, the normally forbidden reflections with $\ell=n$ appear (Fig 2b). Similar imaging behavior has been observed for sodium-beta aluminas and may be attributed to double diffraction (Bevan et al 1979; Sato and Shinozaki 1979). The lattice fringe images of faulted areas exhibit variations in spacings where the faults occur. In large CA_6 grains, syntactic intergrowth regions could be found with a periodicity significantly larger than that of the CA_6 matrix. The fringe spacings were determined using optical reconstruction of the diffraction patterns with the CA_6 phase as an internal reference or by measuring the displacement of the matrix fringes. The periodic intergrowth shown in Fig. 3 had a fringe spacing of 1.554 nm. Non-periodic arrays of syntactic intergrowths were also found as shown

in Fig. 4.

Towards the boundaries of some large grains irregularities in the fringe images could sometimes be found. Examples of the various types of irregularities have been shown in Fig. 5. They include irregular intergrowth, Fig. 5a, gradual disappearance of fringe contracts, Figs. 5b and 5c, or switching to a different fringe spacing, Fig. 5d. Micro-x-ray analysis revealed that these fringe irregularities were linked to a decrease in the CaO contents. While it is difficult to obtain reliable fringe spacings from isolated faults, as pointed out by Self, et al. (1981), comparison of bundels of identical faults to the matrix reference lattice image gave sufficiently accurate results to permit interpretation of the fault types.

By optical reconstruction of the diffraction patterns it was found that the fringe spacing of the syntactic intergrowth shown in Fig. 3 was 3.10 nm. Following Braun (1957), the CA_6 structure can be considered to consist of a sequence of 00.1 blocks, S_4, containing four closely packed oxygen layers and aluminum ions in a spinel arrangement, alternating with a calcium containing layer, B_1, Fig. 6a. This corresponds to the M structure of barium hexaferrite. The images in Fig. 3 may then be interpreted assuming that the heterophase intergrowth has an S_6 spinel block consisting of 6 rather than 4 oxygen planes, alternating with B_1 layers. This would correspond to the W structure of barium hexaferrite, Fig. 6b. The c lattice parameter of the M structure (CA_6), C_M is 2.188 nm (ASTM1975), while that of the intergrowth was determined to be C_W = 3.101 nm if it was assumed that the intergrowth image in Fig. 3 also consisted of 00.2 fringes. One could then write for the [00.1]

spacings of the oxygen planes in the various sub-unit cell blocks of the lattice d_{S4}, d_{S6} and d_{B1}, with $d_{S4} = d_{S6} = d_S$ and $d_{B1} = d_B$ (Fig. 6a and 6b).

$$6\ d_s + 4\ d_B = 2.188\ \text{nm} \quad (M)$$

$$12\ d_s + 4\ d_B = 3.101\ \text{nm} \quad (W)$$

This gives

$$d_s = 0.228\ \text{nm}$$

$$d_B = 0.205\ \text{nm}$$

Since the spinel blocks have interplanar spacings that are somewhat larger than the average [00.1] oxygen plane spacing, one should expect a reflection corresponding to $d_s = 0.228$ nm in the diffraction pattern. Such reflection is indeed found, as shown in Fig. 7. Further support for this interpretation may be seen in Fig. 5d. The fringes switch from the 1.094 nm spacing of the 00.2 reflection of the M phase to a 0.456 nm spacing where Ca is not detected. This spacing corresponds to the {111} spacing of γ-alumina (ASTM 1975). The γ-alumina structure would indeed be expected if Ca was removed from the M structure such that only S_4 blocks remained. The γ-alumina <111> oxygen plane spacing, equal to 0.228 nm as derived from Fig. 5d by optical reconstruction of the diffraction pattern, thus corresponds exactly to the oxygen plane spacing in the spinel blocks of the M and W structures. These observations indicate that the crystallography of CA_x compounds may be described in a manner analogous to that of the barium ferrites. Since we do not have to account for magnetic properties, the simplest notation proposed by Braun (1957) is sufficient. Table 1 gives the possible basic structural units in this system with their c dimension. The crystal structures

that result from combinations of these basic, sub-unit cell structural units are subject to the constraint that the number of B units must equal the number of S units since macroscopic electroneutrality is required. The structures expected in the $CaO-Al_2O_3$ system corresponding to the M,W,X,Y and Z structures of the barium ferrites have been listed in Table 2. The c dimension of a B_mS_n unit can be found simply from

$$C_{BM} = (m+1) \times 0.205 + (2n-1) \times 0.228 \quad (nm)$$

00.1 stacking sequence faulting in the M structure (CA_6) may then be interpreted as intergrowths of single or multiple units of the phases listed in Table 2. Possible single intergrowths and their expected shifting of the 00.2 lattice fringes of the M structure have been listed in Table 3. Additional translations in 00.1 planes, such as described by De Jonghe (1977a) for sodium-beta alumina have not been considered here.

The introduction of 00.1 intergrowths into the CA_6 matrix permits the structure to accommodate C/A compositional changes. F_W, F_x and F_y faults (Table 3) have been indicated in Figs. 2 and 3. F_x and F_y faults are difficult to distinguish on the basis of the matrix fringe shift measurement. However, it can be argued that the higher Ca content of the B_2 layer should lead to a darker fringe. The faults in Fig. 2b, labeled F_x and F_y have been distinguished using this criterion.

The [00.1] variation of the local CaO content is also shown in Fig. 4 for a complex intergrowth configuration of M, X and Y structures. Isolated intergrowths corresponding to F_2 were not found, although stacking sequences of the form $B_1S_4 \cdot B_2S_4$ do occur in the array of M, X and Y phases shown in Fig. 4. Terminating faults may be observed in

Figs. 1 and 5. Such terminations can accommodate compositional gradients in directions normal to [00.1].

It may be noted that the Y structure has a chemical composition that could be obtained equally well by combining units to form $|B_1S_2|$. This structure does, however, not contain a spinel block, since the oxygen plane sequence $AB|B'AB.A'BA|B'...$, is hexagonal. Lattice images corresponding to this possibility could not be found, indicating that a proper spinel block is essential for the stability of the phases under consideration here. The $|B_1S_2|$ structures that have been reported contained additional cations such as Ti^{4+} (Haberey, 1979) or Mg^{2+} (Sato and Hirotsu, 1976).

§3 CONCLUSION

It was found that calcium aluminates have a structure that is more complex than the current phase diagram would indicate. Phases were observed that could be described in a manner analogous to the barium ferrites. These phases have the nominal compositions CA_4, C_2A_{15}, CA_6 and C_2A_7. While the C_3A_{13} phase may be expected it was not found in this investigation. Syntactic intergrowths of the observed phases can accommodate gradients in the C/A composition. The absence of structures containing S_2 blocks suggests that a spinel block S_{2n} with $n \geq 2$ is necessary for the stability of pseudobinary phases related to magnetoplumbite.

ACKNOWLEDGEMENTS

This work was supported by the Division of Materials Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract No. DE-AC03-76SF00098.

REFERENCES

ADELSKÖLD, V., 1938, Arkiv Kemi Min. Geol. 12A, No. 29.

ALLIBERT, M., CHATILLON, C., JACOB, K.T., and LOURTAU, R., 1981, J. Amer. Chem. Soc. 64, 307.

ASTM, 1975, Index to the Powder Diffraction File.

BEVAN, D.J.M., HUDSON, B., and MOSELEY, P.T., 1974, Mat. Res. Bull., 9, 1073.

BRAUN, P.B., 1957, Philips Res. Rep., 12, 491.

COCKAYNE, B., and LENT, B., 1979, 46, 467.

DE JONGHE, L.C., 1977a, J. Mat. Sci., 12, 497.

DE JONGHE, L.C., 1977b, Mat. Res. Bull., 6, 29.

FILONENKO, N.E., and LAVROV, J.V., 1949, Dok. Akad. Nauk. SSSR, 66, 673.

GENTILE, A.L., and FOSTER, W.R., 1963, J. Amer. Ceram. Soc., 46, 74.

HABEREY, F., and VELICESCU, M., 1974, Acta Cryst., B30, 1507.

JEPPS, N.W., SMITH, D.J., and PAGE, T.F., 1979, Acta Cryst., A35, 916.

LAGERQUIST, U.K., HALMARKS, S., and WESTGREN, A., 1937, Z. Anorg. Allgem. Chem., 234, 1.

NURSE, R.W., WELCH, J.H., and MAJUNDAR, J.A., 1965a, Trans. Brit. Ceram. Soc., 64, 323.

NURSE, R.W., WELCH, J.H., and MAJUNDAR, J.A., 1965b, ibid., 409.

SATO, H., and SHINOZAKI, S., 1974, Mat. Res. Bull., 9, 679.

SATO, H., and HIROTSU, Y., 1976, Mat. Res. Bull., 11, 1307.

SELF, P.G., BHADESHIA, H.D.K.H., and STOBBS, W.M., 1981, Ultra Microscopy, 6, 29.

SHEPHERD, E.S., RANKIN, G.A., and WRIGHT, F.E., 1909, Amer. J. Sci., 28, 293.

Table 1. Basic structural elements.

Structural Elements	Notation[a]	c dimension in nm[b]	Oxygen Stacking Sequence
Single Ca containing layer	B_1	0.410	A'
Double Ca containing layer	B_2	0.615	$A'B'$
Multiple spinel layer	s_{2n}	(2n-1)x0.228	$\frac{AB}{1}\frac{CA}{2}\frac{BC}{3}..\frac{ABC}{n}$

[a]The symbolism follows Braun (1957)

[b]The c spacings were calculated or derived from observed lattice spacings.

Table 2. Structural parameters and stacking sequence of periodic structures of calcium aluminates.

Type[a]	Composition	Wt % CaO	Unit cell Structure	c dimension of unit cell in nm	oxygen stacking sequence
M	CA_6	8.4	$2\|B_1S_4\|$	2.188	AB|A´BACB.C´BCAB|A´BA
W	CA_9	5.7	$2\|B_1S_6\|$	3.101	AB|A´BACBAC.A´CABCAB|A´BA
X	C_2A_{15}	6.8	$3\|B_1S_4B_1S_4\|$	7.932	AB|A´BACB.C´BCABCA.C´ACBABC.B´CBAC.A´CABCAB|A´B
Y	C_2A_7	13.6	$3\|B_2S_4\|$	3.897	AB|A´B´ABCA.C´A´CABC.B´C´BCAB|A´B´A
Z	C_3A_{13}	11.3	$2\|B_1S_4.B_2S_4\|$	4.786	AB|A´BACB.C´B´CABC.A´CABC.B´C´BCAB|A´BA

[a]Nomenclature following Braun (1957).

Table 3. Fault parameters for $CA_6(M)$ matrix.

Fault Type	Fault Structure	00.2 Lattice Image Shift of M Phase
F_W	$\lvert B_1S_6 \cdot B_1S_6 \rvert$	3.101
F_x	$\lvert B_1S_4 \cdot B_1S_6 \rvert$	2.644
F_y	$\lvert B_2S_4 \cdot B_2S_4 \rvert$	2.598
F_z	$\lvert B_1S_4 \cdot B_2S_4 \rvert$	2.393
$F_{2n}(n>3)$	$\lvert B_1S_{2n} \rvert$	$2d_B+(2n-1)\ d_s$ (spinel intergrowth)

Figure Captions

Fig. 1 (a) CA_6 containing syntactic intergrowth phases on 00.1 planes, bright field (BF); some terminating intergrowths have been arrowed.

(b) Selected area diffraction pattern of area shown in Fig. 1a. The electron beam is parallel to the $1\bar{1}.0$ zone axis.

Fig. 2 Lattice fringe images and selected area diffraction pattern of faulted CA_6.

(a) BF image showing 00.2 fringes of the CA_6 phase, and F_W intergrowths.

(b) BF image showing 00.1 fringes of the CA_6 phase with F_x and F_y intergrowths.

Fig. 3 (a) M and W syntactic phases, and F_W intergrowth.

(b) Optical reconstruction of the M and W diffraction patterns. This permits accurate determination of the 00.1 lattice parameters of the W phase, with M as a reference.

Fig. 4 (a) Non-periodic F_y intergrowth forming a transition zone between the $M(CA_6)$ and the $Y(C_2A_7)$ phase.

(b) Schematic representation of the local CaO content in the Y-M transition zone imaged in Fig. 4a.

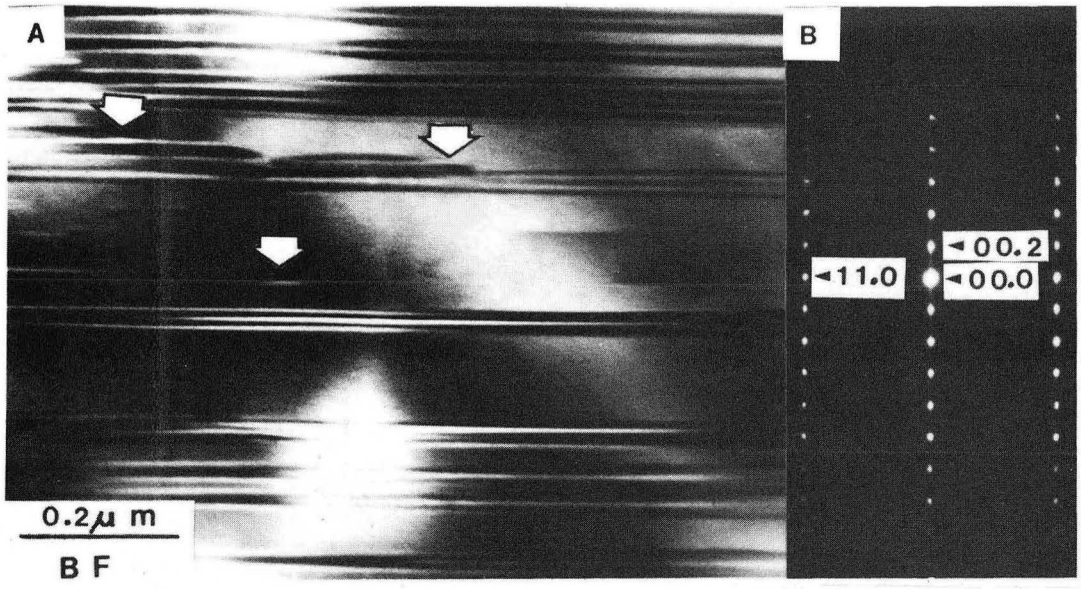
Fig. 5 (a) Irregular lattice fringe images due to terminating M intergrowths in a W Matrix. The energy dispensive x-ray spectra of the marked regions are also shown.

(b) Terminating F_{2n} intergrowths in a transition zone between a CA_6 and CaO free region.

(c) Transition of M phase to γ-alumina. The identification of the γ-phase comes from optical reconstruction of the diffraction patterns of the correspondingly marked areas, as well as from the energy dispensive x-ray analysis.

Fig. 6 Projected structures of M and W unit cells. The spinel blocks S_4 and S_6 and the calcium containing interlayers B_1, have been marked, as well as the oxygen plane sequence (after Braun, 1957).

Fig. 7 00.l reflections of M phase showing extra reflection corresponding to the spinel block oxygen plane spacing d_s = 0.228 nm. The 00.10 reflection of the M phase corresponds to 0.2188 nm.



XBB 824-3405

Fig. 1

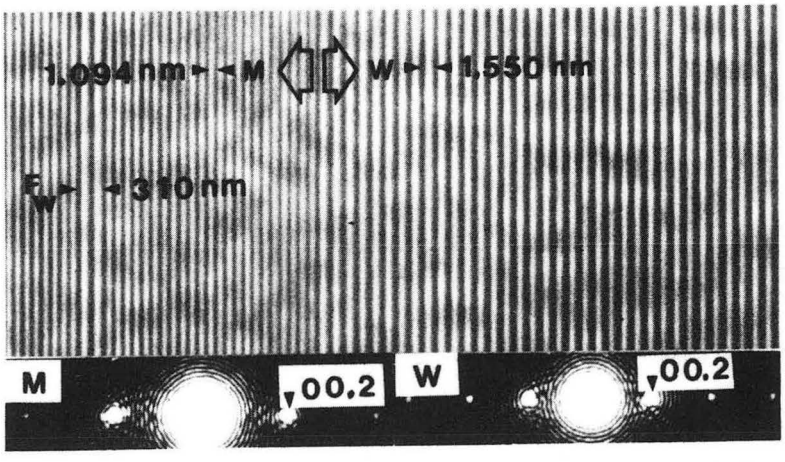


Fig. 2

XBB 824-3404

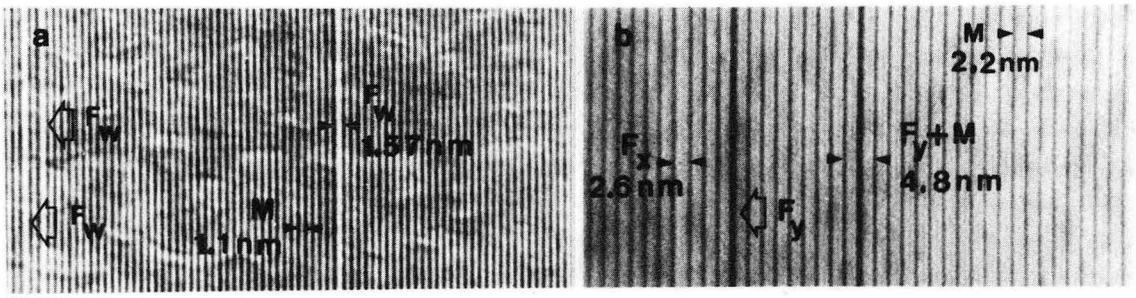


Fig. 3

XBB 824-3406

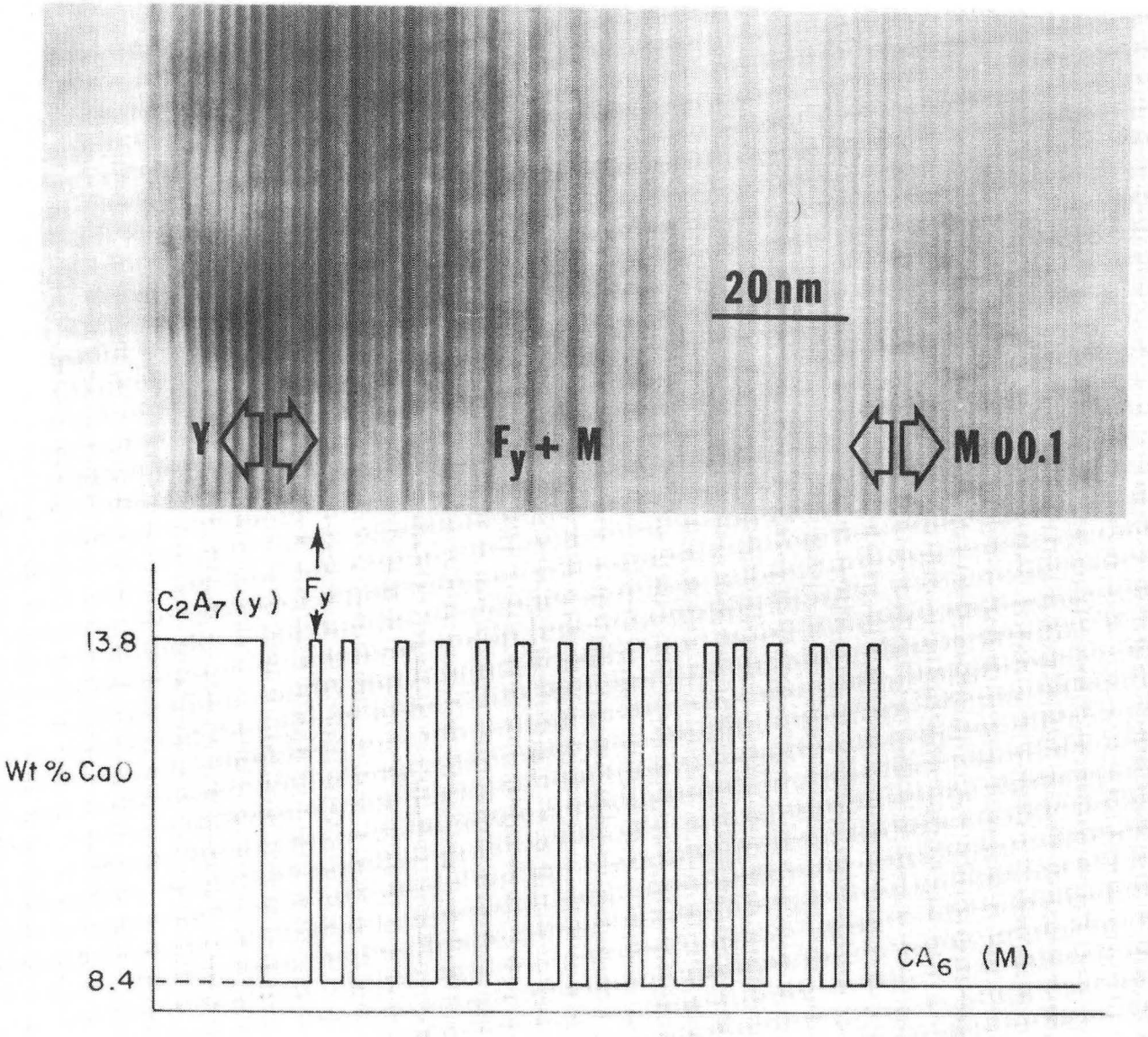
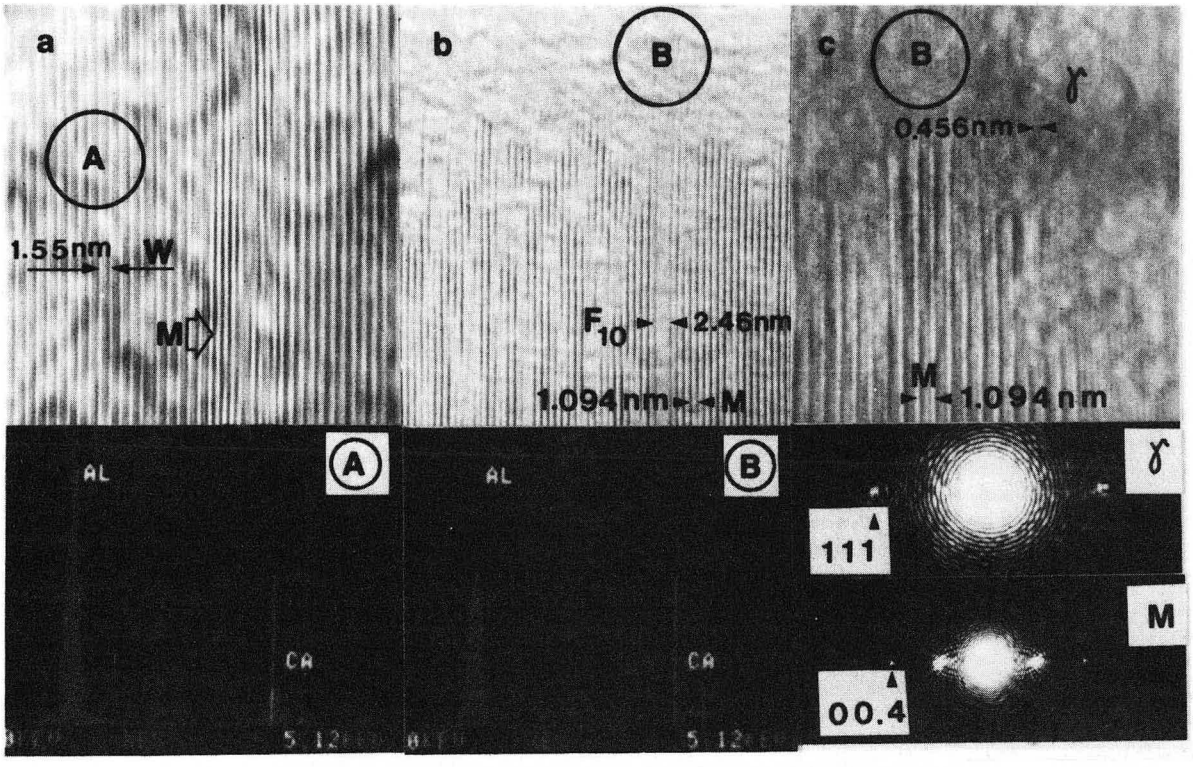


Fig. 4

XBB 824-3978



XBB 824-3398

Fig. 5

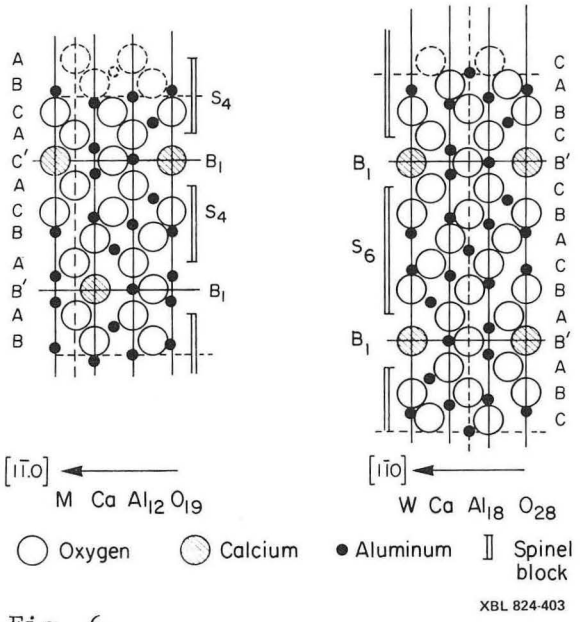

A
B
C
A
C′
A
C
B
A
B′
A
B
S4
B1
S4
B1
[1$\bar{1}$0]
M Ca Al12 O19
C
A
B
C
B1
B′
C
B
A
S6
C
B
A
B1
B′
A
B
C
[1$\bar{1}$0]
W Ca Al18 O28
Oxygen
Calcium
Aluminum
Spinel block
XBL 824-403

Fig. 6

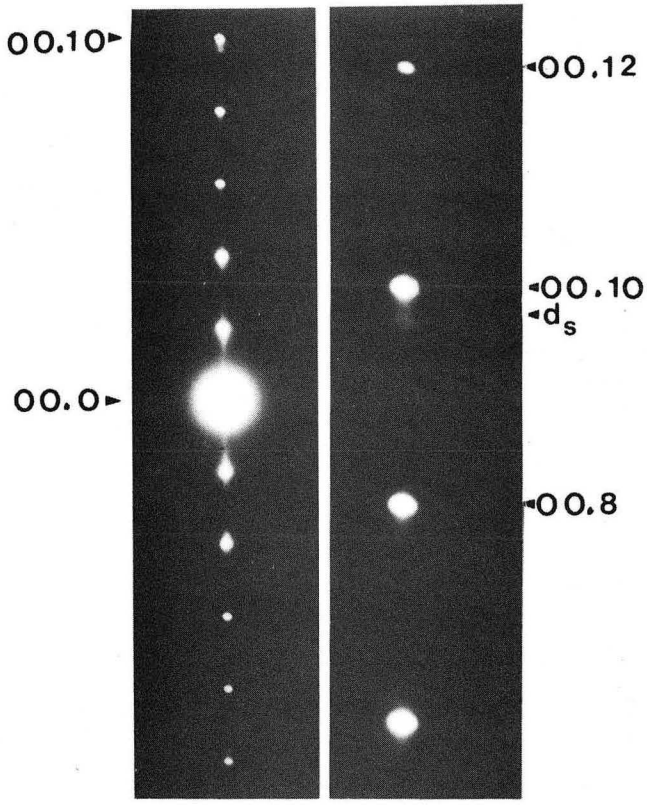


Fig. 7 XBB 824-3407

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720