Investigations on the Crystal Structure and the Stability Field of FCAM-I ($\text{Ca}_3\text{MgAl}_6\text{Fe}_{10}\text{O}_{28}$), an Iso-structure to SFCA-I

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In a study on parts of the system Fe_2O_3 - CaO - Al_2O_3 - MgO , the previously unknown compound $\text{Ca}_3\text{MgAl}_6\text{Fe}_{10}\text{O}_{28}$ or FCAM-I (iso-structural with SFCA-I) has been synthesized. The two principal aims of our investigations have been (i) analysis of the stability field of the new phase as a function of T and $f\text{O}_2$ and (ii) determination of its crystal structure. Two experimental series in air and under controlled oxygen fugacity *via* the hematite-magnetite buffer were conducted. Pure polycrystalline FCAM-I has been obtained at 1463.15 K (1190 °C) in air. While increasing the temperature from 1573.15 K to 1673.15 K (1300 °C to 1400 °C), the FCAM-I phase breaks down forming a variety of new compounds depending on T and $f\text{O}_2$. $\text{Ca}_3\text{MgAl}_6\text{Fe}_{10}\text{O}_{28}$ has a triclinic crystal structure (space group $P\bar{1}$). Basic crystallographic data are as follows: $a = 10.2980(4)$ Å, $b = 10.4677(4)$ Å, $c = 11.6399(4)$ Å, $\alpha = 94.363(3)^\circ$, $\beta = 111.498(3)^\circ$, $\gamma = 109.744(3)^\circ$, $V = 1069.81(7)$ Å³, $Z = 2$.

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I. INTRODUCTION

SFCA is an acronym that was coined by Hancart *et al.*^[1] rather generally for silico-ferrites of calcium and aluminum in order to describe the most important bonding constituents forming during the production of industrial iron ore sinters. Later, in a sequence of papers^[2–5] Mumme and co-workers used this term more specifically for the description of several crystallographically different but structurally closely related phases whose chemical composition can be given as $\text{M}_{14+6n}\text{O}_{20+8n}$ (where $\text{M} = \text{Si}, \text{Fe}, \text{Al}, \text{Ca}, \text{Mg}$, and $n = 0$ to 1). From a structural point of view, these compounds form a homologous series and the members with $n = 0$ and $n = 1$ were designated SFCA and SFCA-I, respectively. Furthermore, a SFCA-II phase has been mentioned representing an intermediate of SFCA and SFCA-I.^[6] The stability regions of these compounds are only partially well characterized using *in-situ* synchrotron X-ray diffraction. The formation

temperature^[6] of SFCA-I *via* the reaction of SFCA + Fe_2O_3 was determined at 1392.15 K (1119 °C) by $p\text{O}_2 = 5 \times 10^{-3}$ atm. Webster *et al.*^[6] postulated that the differences in the temperature of formation can directly be related to variations in the oxygen fugacity and/or heating rate.

SFCA and SFCA-I show complex solid solution series involving a substitution mechanism based on the exchange of $2(\text{Fe}^{3+}, \text{Al}^{3+}) \leftrightarrow (\text{Ca}^{2+}, \text{Fe}^{2+}) + \text{Si}^{4+}$,^[7] in which the increase of Al_2O_3 concentration has a positive effect of the stability field of SFCA-I at lower temperatures.^[6] Furthermore, an increasing replacement of Fe^{3+} by Al^{3+} with increasing temperature has been observed. Depending on the chemical system, the two phases SFAC and SFCA-I can coexist in which SFCA-I is potentially more stable at higher temperatures. SFAC decomposes around 1743.15 K (1470 °C) completely and is progressively unstable with decreasing Al_2O_3 content.^[7] Mumme^[5] proposed that the three homologous SFCA structure-types have a much more limited temperature range than the so far suggested 973.15 K to 1743.15 K (700 °C to 1470 °C).

Triggered by previous studies on SFCA-related materials, this investigation focused on the influence of Mg incorporation in a silicon-free SFCA-I analogue. Adapting the nomenclature suggested by Mumme, the Mg-containing compounds will be labeled “FCAM-I.” According to Kalenga and Garbers-Craig,^[8] the physico-chemical properties of iron ore sinters depend noticeably on the MgO content, which is due to the

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addition of Mg-containing fluxes such as dolomite or fused MgO during the sintering process. The magnesium oxide concentration, for example, is positively correlated with the abrasion and tumble indices as well as the coke rate. The present study focuses on the structural investigations on FCAM-I or $\text{Ca}_3\text{MgAl}_6\text{Fe}_{10}\text{O}_{28}$ (corresponding to the Si-free version of SFCA-I with an MgO content of up to 2.8 mol pct). Moreover, based on the quaternary system $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-CaO-MgO}$, a systematic examination of the $T\text{-}f\text{O}_2$ stability of this FCAM-I phase with respect to the coexisting phase assemblages was performed.

II. EXPERIMENTAL METHODS

A. Synthesis of FCAM-I

Synthesis experiments of silicon-free SFCA-I with a magnesium substitution of one atom per formula unit (apfu) were based on the molar ratio $\text{CaO:MgO:Al}_2\text{O}_3\text{:Fe}_2\text{O}_3 = 3:1:3:5$, which corresponds to a composition of $\text{Ca}_3\text{MgAl}_6\text{Fe}_{10}\text{O}_{28}$. Starting materials for the solid-state reactions were dried Fe_2O_3 (>99 pct), $\gamma\text{-Al}_2\text{O}_3$ (99.997 pct), MgO (99.998 pct), and CaCO_3 (>99 pct) which were checked for phase purity using XRPD.

decarbonization. The temperature conditions as well as the heating ramps were the same as in the previous “in-air” experiments. In order to monitor temperature conditions as precisely as possible, a second external Pt-Pt₉₀Rh₁₀ thermocouple was placed on top of the sample.

After the experiments, the buffer assemblage was analyzed by X-ray powder diffraction. The ratio between hematite and magnetite was calculated by quantitative phase analysis based on the Rietveld method using the software suite TOPAS 4.2.^[9] Between 1473.15 K and 1683.15 K (1200 °C and 1410 °C), hematite (H) and magnetite (M) coexist in the experiments. The resulting oxygen fugacity was calculated by the model Reaction (A)

and the following thermodynamic relations (B)

$$\Delta G_f^0 = \Delta H_f^0 + T\Delta S_f^0 \quad K = e^{\frac{-\Delta G_f^0}{RT}} \rightarrow -\log K = \log f_{\text{O}_2} \approx \log P_{\text{O}_2}^{(1)}, \quad [\text{B}]$$

at standard condition (1 atm) by using the thermodynamic data from Robie and Hemingway.^[10]

Fe_2O_3	$\Delta G_{f,298}^0 = -744400 \text{ J/mol}$	$\Delta H_{f,298}^0 = -826200 \text{ J/mol}$	$\Delta S_{298}^0 = 87.40 \text{ J/mol K}$
Fe_3O_4	$\Delta G_{f,298}^0 = -1012700 \text{ J/mol}$	$\Delta H_{f,298}^0 = -1115700 \text{ J/mol}$	$\Delta S_{298}^0 = 146.14 \text{ J/mol K}$
O_2			$\Delta S_{298}^0 = 205.15 \text{ J/mol K}$

Subsequently, the separate powders were mixed and homogenized under ethanol in a ball mill for 45 minutes.

Approximately 0.5 g of the powdered mixture was dried again and pressed into pellets with a diameter of 13 mm. In a first set of experiments, the pellets were sintered in air in the temperature range between 1473.15 K and 1673.15 K (1200 °C and 1400 °C) using an open Pt crucible placed in a chamber furnace. The samples were heated from room temperature up to the respective maximum temperature with a heating rate of 1.5 K/minutes. 20 K below the final temperature, the heating ramp was reduced to 0.5 K/minutes in order to avoid overheating of the sample. The maximum temperature was held for 24 hours. Afterwards, the samples were rapidly quenched to room temperature by placing the bottom of the Pt crucible into a water bath.

The second series of experiments was conducted using a platinum double-capsule geometry (Figure 1) controlling the oxygen fugacity *via* the hematite-magnetite buffer. The assembly consists of an outer Pt capsule with a length of 25 mm and an outer diameter of 5 mm containing the inner Pt capsule surrounded by the $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ buffer. The container was filled only up to two-thirds of the sample volume. The inner capsule contains the pressed starting mixture which was previously heated to 1073.15 K (800 °C) for 12 hours for

At 1473.15 K (1200 °C), the hematite/magnetite ratio corresponds to 99:1 (HM). Above these temperatures, magnetite starts to form and the hematite-magnetite buffer is in equilibrium. The calculated $\log_{10} P_{\text{O}_2}$ increases from -3.67 at 1473.15 K (1200 °C) to -1.48 at 1683.15 K (1410 °C). Exceeding 1683.15 K, hematite disappears and the experiments move into the stability field of magnetite (0.0 pct H to 100.0 pct M). Consequently, P_{O_2} drops down to $\log_{10} P_{\text{O}_2} < -1.13$ at 1723.15 K (1450 °C).

Single crystals of FCAM-I have been obtained somewhat serendipitously during previous experiments aiming on the preparation of Mg-containing C_2F with a composition $\text{Ca}_{1.9}\text{Mg}_{0.1}\text{Fe}_2\text{O}_5$ in open corundum crucibles in air using the same starting materials as for the solid-state reactions. Two grams of the stoichiometrically weighed powders were homogenized in an agate mortar, transferred into an open 50 ml corundum crucible, and placed in a resistance-heated chamber furnace. Heating experiments were performed in air. The sample container was fired from 373.15 K (100 °C) with a rate of 200 K/hour to 1623.15 K (1350 °C), subsequently cooled with 1 K/hour to 1573.15 K (1300 °C), and finally quenched to ambient conditions. First visual inspection of the synthesis product revealed that the sample was highly crystalline. Furthermore, it was obvious that (i) the crystals had grown

Fig. 1—Outline of the platinum double-capsule geometry.

from a melt phase and (ii) reactions between the educts and the Al_2O_3 component of the crucible had occurred. The simultaneous presence of optically transparent and almost opaque crystals pointed to the existence of a complex phase mixture. The colors of the crystals ranged from honey-colored through reddish-brown to dark-brown or almost black. Concerning the sizes, the dark-brown compound was especially conspicuous: the lath-shaped crystals reached maximum dimensions of up to 1 mm and proved to be FCAM-I. Furthermore, single crystals of $\text{Ca}(\text{Al,Fe})\text{O}_4$ and $\text{Ca}(\text{Al,Fe})_4\text{O}_7$ could be detected.

Subsequently, the resulting FCAM-I samples were analyzed by X-ray powder diffractometry, single-crystal X-ray diffraction, and EMPA.

B. X-ray Powder Diffraction

The BRUKER-AXS D8-Advance powder diffractometer used (Bragg–Brentano geometry with θ – θ coupling) is equipped with parallel beam optics and an energy-dispersive Si(Li) semiconducting Sol-X detector yielding $\text{CuK}\alpha_1$ and $\text{CuK}\alpha_2$ radiation. The settings for the recorded powder diffraction data were 40 kV and 40 mA and a LYNXEYE™ silicon strip detector. Data were collected at ambient temperature in the 2θ range

between 3 and 100 deg with a counting time of 10 seconds/step and a step size of 0.02 deg 2θ . For phase identification, LeBail fits using TOPAS 4.2^[9] and the current version of the PDF-4+^[11] database were used. The peak profiles in the fits were calculated using the fundamental parameter approach.^[12] The background was simulated by Chebyshev polynomials of the 5th order.

C. Electron Microprobe Analysis

In order to obtain the compositions and to study phase relations of the experiments, part of the synthesized material was embedded in epoxy resin and polished with diamond paste (10, 5, and 1 μm grain size). Electron microprobe analysis in wavelength dispersive mode was performed using a JEOL JXA SUPERPROBE 8100. Measurement conditions were 15 kV acceleration voltage and 10 nA beam current. The measurement time for the peaks was 20 and 10 seconds for the background. A total number between 1 and 3 spots in various regions of the crystals were analyzed. The standard reference materials used for analysis of Ca, Al, Fe, and Mg were diopside (Ca), corundum (Al), hematite (Fe), magnetite (Fe), and magnesia (Mg). Intensities obtained were corrected for electron scattering, absorption, and fluorescence radiation (so-called ZAF correction). Finally, the $\text{Fe}^{2+}/\text{Fe}_{\text{tot}}$ ratio was calculated from the total iron content based on the crystal-chemical formula obtained from EMPA measurements and charge balance considerations.

D. Single-Crystal X-ray Diffraction

The basic crystallographic data at ambient temperature (293.15 K (20 °C)) of a sample retrieved from the single-crystal growth experiment were obtained by single-crystal diffraction using an Oxford Diffraction Gemini R Ultra single-crystal diffractometer. Therefore, a reddish fragment ($210 \times 100 \times 90 \mu\text{m}$) of a single crystal was mounted on top of a glass fiber. For the structure determination of the triclinic compound, a total of 583 frames using ω -scans with 1 deg scan width per frame covering a hemisphere of reciprocal space were collected.

The integration and data reduction were performed using the CrysAlis Pro software package^[13] including corrections for Lorentz and polarization effects. Furthermore, an analytical absorption correction using accurately measured external faces has been employed. X-ray scattering factors together with real and imaginary coefficients for anomalous dispersion were taken from the International Tables for Crystallography, Vol. C.^[14] The structure was solved in space group $P\bar{1}$ using direct methods *via* the program SIR2004.^[15] The final least-squares refinement using anisotropic displacement parameters for all atoms was performed with the program SHELX-97^[16] embedded in the WinGX software suite.^[17] The calculations converged to a residual of $R_1 = 0.0258$ for all reflections with $I > 2\sigma(I)$ using 450 parameters (Table I).

Table I. Crystal and Structure Refinement Data for Ca₃MgAl₆Fe₁₀O₂₈ (FCAM-I)

Empirical formula	Ca _{2.90} Mg _{0.95} Fe _{10.11} Al _{5.99} O ₂₈	
Crystal system	triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	$a = 10.2980(4) \text{ \AA}$ $b = 10.4677(4) \text{ \AA}$ $c = 11.6399(4) \text{ \AA}$	$\alpha = 94.363(3)^\circ$ $\beta = 111.498(3)^\circ$ $\gamma = 109.744(3)^\circ$
Volume	1069.81(7) $\text{\AA}^3$	
Z	2	
Density (calculated)	4.078 g/cm ³	
Absorption coefficient	7.803 mm ⁻¹	
F(0 0 0)	1452	
Intensity measurements		
Crystal size	0.21 × 0.10 × 0.09 mm ³	
Theta range for data collection	3.18 to 32.82 deg	
Diffractometer	Oxford Diffraction Gemini R Ultra	
Monochromator	Graphite	
Data collection temperature	293.15 K (20 °C)	
Wavelength	0.71073 $\text{\AA}$	
Index ranges	$-14 \leq h \leq 15$, $-15 \leq k \leq 15$, $-17 \leq l \leq 17$	
Scan type	ω -scans	
Scan width	1 deg	
Exposure time	20.0 s/frame	
Reflections collected	21522	
Independent reflections	7387 [R(int) = 0.0258]	
Observed reflections [I > 2 σ (I)]		
Completeness to theta = 32.82 deg	93.1 pct	
Max. and min. transmission	0.422 and 0.624	
Refinement of the structures		
Refinement method	Full-matrix least-squares on F ²	
Parameters/restraints	450/0	
Goodness-of-fit on F2	1.006	
Final R indices [I42 σ (I)]	R1 = 0.0258, wR2 = 0.0595	
R indices (all data)	R1 = 0.0346, wR2 = 0.0635	
Largest diff. peak and hole	0.579 and -1.035 e. $\text{\AA}^{-3}$	

Since (i) the assignment of more than two chemical species to a specific position is mathematically undetermined and (ii) Mg and Al have almost identical scattering factors for X-rays, for site occupancy analysis on the different *octahedral* and *tetrahedral* sites the following procedure has been selected: Initially, the magnesium content was completely neglected and the total scattering power for each site was obtained by allowing for a potential Fe ↔ Al substitution under the assumption. For two of the three calcium positions in the asymmetric unit site, occupancy refinements indicated full occupation within 2 standard uncertainties. However, for the remaining “Ca-position” M2 the total scattering power was significantly less than 20 electrons pointing to a more complex cation distribution. A detailed analysis of the site populations, *i.e.*, the assignment of different chemical species (Fe, Al, Mg, Ca) to each position was performed a posteriori using the program OccQP^[18] where the full information from chemical analysis, refined total scattering powers for the positions, and bond distances is considered to find an optimal distribution. The mathematical algorithm is a quadratic numerical approach based on the least-squares method and a weighted linear system. The strength of the program is the minimization of the residual between formal and apparent valences for an acceptable crystal-chemically solution.^[18]

Analysis of the atomic coordinates has proven the crystal structure of FCAM-I to be iso-structural with SFCA-I. For sake of clarity, labeling of the atoms in the asymmetric unit was therefore performed according to the already published crystal structure of SFCA-I.^[4] The refined atomic coordinates, equivalent isotropic and anisotropic displacement parameters, as well as selected interatomic distances are listed in Tables II, III, and IV. Figures showing structural details were prepared using the program ATOMS6.4.^[19]

E. TGA: DTA Analysis

Approximately 14 mg of the starting mixture was studied in an open platinum crucible by thermogravimetric (TGA) and differential thermal (DTA) analysis. The crucible was made out of a Pt tube with a diameter of 3 mm which was placed in an open corundum crucible (100 ml). The experiment was performed in a Setaram Setsys Evolution 2400 thermal analyzer. The device is coupled with a mass spectrometer OmniStar GSD-301 02 (Pfeifer Vacuum, Asslar, Germany). The sample holder is equipped with Pt/Pt₉₀-Rh₁₀ thermocouples. Temperature was increased with a ramp of 5 K per minute from room temperature to 1773.15 K (1500 °C). The experiments were done in air, in a helium atmosphere (99.999 pct), and in an oxygen

Table II. Atomic Coordinates, Site Occupancies, and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2$) for $\text{Ca}_{2.90}\text{Mg}_{0.95}\text{Fe}_{10.11}\text{Al}_{5.99}\text{O}_{28}$ (FCAM-I)

Atom	Site Populations	x	y	z	U(eq)
M1	100.0 pct Ca	0.07927(4)	0.68269(4)	0.16664(4)	0.0096(1)
M2	44.7 pct Ca + 23.2 pct Mg + 27.6 pct Fe(III) + 4.5 pct Vac	0.47000(5)	0.11094(4)	0.92148(4)	0.0113(1)
M3	100.0 pct Ca	0.09151(4)	0.15216(4)	0.16917(4)	0.0093(1)
M4	4.3 pct Ca + 63.7 pct Fe(III) + 32.0 pct Al	0.31505(4)	0.03264(3)	0.63185(3)	0.0057(1)
M5	4.0 pct Ca + 18.3 pct Mg + 77.7 pct Fe (III)	0.17526(3)	0.46216(3)	0.34792(3)	0.0060(1)
M6	11.6 pct Ca + 14.5 pct Mg + 73.9 pct Fe(III)	0.54234(3)	0.39830(3)	0.08589(3)	0.0073(1)
M7	5.3 pct Ca + 75.8 pct Fe(III) + 18.9 pct Al	0.07597(3)	0.78956(3)	0.64607(3)	0.0056(1)
M8	5.2 pct Ca + 77.2 pct Fe(III) + 17.6 pct Al	0.24200(3)	0.74532(3)	0.48592(3)	0.0059(1)
M9	2.9 pct Ca + 80.0 pct Fe(III) + 17.1 pct Al	0.62339(3)	0.67740(3)	0.22296(3)	0.0066(1)
M10	6.4 pct Ca + 2.9 pct Mg + 76.6 pct Fe(III) + 14.1 pct Al	0.24481(3)	0.24849(3)	0.48759(3)	0.0059(1)
M11	1.1 pct Ca + 70.1 pct Fe(III) + 28.8 pct Al	0.60176(4)	0.18707(3)	0.22722(3)	0.0062(1)
M12	4.6 pct Ca + 74.3 pct Fe(III) + 21.1 pct Al	0.43009(3)	0.71475(3)	0.35367(3)	0.0061(1)
T1	7.4 pct Mg + 61.6 pct Fe(III) + 31.0 pct Al	0.00895(4)	0.08887(3)	0.63489(3)	0.0048(1)
T2	7.1 pct Mg + 60.8 pct Fe(III) + 32.1 pct Al	0.37643(4)	0.02167(3)	0.36888(3)	0.0050(1)
T3	14.2 pct Mg + 85.8 pct Fe(III)	0.13162(3)	0.47389(3)	0.63639(3)	0.0061(1)
T4	9.7 pct Fe(III) + 90.3 pct Al	0.24414(6)	0.48114(5)	0.07938(5)	0.0054(2)
T5	7.5 pct Mg + 92.5 pct Fe(III)	0.49581(3)	0.40673(3)	0.36528(3)	0.0054(1)
T6	2.5 pct Fe(III) + 97.5 pct Al	0.83678(6)	0.31575(6)	0.08761(6)	0.0053(2)
T7	1.1 pct Fe(III) + 98.9 pct Al	0.17504(6)	0.19288(6)	0.92854(6)	0.0059(2)
T8	100.0 pct Al	0.25244(6)	0.97725(6)	0.07951(6)	0.0063(1)
O1		0.02051(15)	0.69413(14)	0.77339(14)	0.0082(3)
O2		0.25031(16)	0.03582(15)	0.22200(14)	0.0106(3)
O3		0.37035(15)	0.12778(14)	0.50185(14)	0.0094(3)
O4		0.03621(16)	0.18201(15)	0.78237(14)	0.0107(3)
O5		0.86929(16)	0.12673(15)	0.50040(14)	0.0098(3)
O6		0.75151(15)	0.44212(14)	0.77525(14)	0.0088(3)
O7		0.42918(15)	0.90521(14)	0.62824(14)	0.0096(3)
O8		0.63392(15)	0.37391(14)	0.51415(14)	0.0090(3)
O9		0.12245(16)	0.52446(14)	0.95313(14)	0.0124(3)
O10		0.56431(16)	0.95714(16)	0.91126(15)	0.0160(3)
O11		0.19957(16)	0.15867(15)	0.63047(14)	0.0097(3)
O12		0.31502(16)	0.83151(14)	0.36319(14)	0.0103(3)
O13		0.87922(16)	0.63433(14)	0.51557(14)	0.0106(3)
O14		0.19770(16)	0.67354(15)	0.62966(14)	0.0119(3)
O15		0.50064(16)	0.31236(15)	0.22707(15)	0.0131(3)
O16		0.43515(15)	0.39563(14)	0.63273(14)	0.0095(3)
O17		0.66010(16)	0.27293(16)	0.09830(15)	0.0153(3)
O18		0.04882(15)	0.09912(14)	0.36241(14)	0.0093(3)
O19		0.35547(16)	0.25338(16)	0.92687(15)	0.0136(3)
O20		0.83950(16)	0.70089(14)	0.95756(14)	0.0108(3)
O21		0.18497(18)	0.79851(15)	0.03997(14)	0.0159(3)
O22		0.13276(16)	0.03118(14)	0.96645(14)	0.0122(3)
O23		0.72271(18)	0.55471(16)	0.22358(17)	0.0196(4)
O24		0.48409(16)	0.19703(14)	0.75666(14)	0.0105(3)
O25		0.29603(16)	0.34066(14)	0.35872(14)	0.0100(3)
O26		0.56961(16)	0.46834(15)	0.91821(15)	0.0135(3)
O27		0.72711(15)	0.06669(14)	0.24251(14)	0.0102(3)
O28		0.93418(17)	0.41015(15)	0.64214(15)	0.0136(3)

Cation distributions have been calculated with the OccQP program.^[18] U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

atmosphere (99.995 pct) using a gas flow of 20 ml per hour.

III. RESULTS

A. Crystal Structure

The crystal structure of FCAM-I is iso-structural with SFCA-I, whose structural features have been previously determined by Mumme *et al.*^[4] Basic crystallographic data on FCAM-I are as follows: triclinic symmetry,

space group $P\bar{1}$, $a = 10.2940(3) \text{ \AA}$, $b = 10.4393(3) \text{ \AA}$, $c = 11.5977(6) \text{ \AA}$, $\alpha = 94.342(6) \text{ deg}$, $\beta = 111.611(6) \text{ deg}$, $\gamma = 109.617(3) \text{ deg}$, $V = 1069.81(7) \text{ \AA}^3$, $Z = 2$. The structure can be built up from an alternating sequence of two different types of layers running parallel to (20-1) (see Figure 2(a)).

Layer-type I contains MO_6 octahedra as well as TO_4 tetrahedra (T: Al, Fe, Mg), whereas layer II is exclusively based on MO_6 octahedra (M: Ca, Fe, Al, Mg). Views of both sheets in projections perpendicular to the

Table III. Anisotropic Displacement Parameters for $\text{Ca}_{2.90}\text{Mg}_{0.95}\text{Fe}_{10.11}\text{Al}_{5.99}\text{O}_{28}$. The Anisotropic Displacement Factor Exponent Takes the Form: $-2\pi^2[h^2a^{*2}U_{11} + \dots + 2hk a^* b^* U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
M1	0.0092(2)	0.0096(2)	0.0100(2)	0.0030(1)	0.0035(2)	0.0043(2)
M2	0.0188(2)	0.0102(2)	0.0075(2)	0.0026(2)	0.0049(2)	0.0093(2)
M3	0.0099(2)	0.0084(2)	0.0098(2)	0.0017(1)	0.0046(2)	0.0033(1)
M4	0.0057(2)	0.0042(2)	0.0065(2)	0.0012(1)	0.0025(1)	0.0013(1)
M5	0.0057(2)	0.0053(2)	0.0066(2)	0.0014(1)	0.0026(1)	0.0016(1)
M6	0.0075(2)	0.0063(2)	0.0072(2)	0.0013(1)	0.0018(1)	0.0033(1)
M7	0.0046(2)	0.0062(2)	0.0064(2)	0.0021(1)	0.0026(1)	0.0021(1)
M8	0.0062(2)	0.0059(2)	0.0055(2)	0.0009(1)	0.0027(1)	0.0022(1)
M9	0.0076(2)	0.0060(2)	0.0067(2)	0.0013(1)	0.0036(1)	0.0026(1)
M10	0.0052(2)	0.0060(2)	0.0060(2)	0.0017(1)	0.0021(1)	0.0021(1)
M11	0.0060(2)	0.0061(2)	0.0062(2)	0.0018(1)	0.0024(1)	0.0021(1)
M12	0.0052(2)	0.0062(2)	0.0070(2)	0.0012(1)	0.0031(1)	0.0019(1)
T1	0.0044(2)	0.0048(2)	0.0047(2)	0.0011(1)	0.0017(1)	0.0017(1)
T2	0.0048(2)	0.0052(2)	0.0050(2)	0.0009(1)	0.0023(1)	0.0019(1)
T3	0.0056(2)	0.0052(2)	0.0081(2)	0.0017(1)	0.0033(1)	0.0022(1)
T4	0.0052(3)	0.0053(3)	0.0056(3)	0.0008(2)	0.0025(2)	0.0018(2)
T5	0.0050(1)	0.0054(2)	0.0064(2)	0.0018(1)	0.0027(1)	0.0021(1)
T6	0.0047(3)	0.0058(3)	0.0054(3)	0.0019(2)	0.0018(2)	0.0024(2)
T7	0.0050(3)	0.0061(3)	0.0065(3)	0.0019(2)	0.0025(2)	0.0019(2)
T8	0.0056(3)	0.0064(3)	0.0069(3)	0.0014(2)	0.0027(2)	0.0023(2)
O1	0.0076(6)	0.0082(6)	0.0080(7)	0.0021(5)	0.0028(5)	0.0027(5)
O2	0.0126(7)	0.0132(7)	0.0084(7)	0.0026(6)	0.0045(6)	0.0076(6)
O3	0.0087(6)	0.0108(7)	0.0088(7)	0.0021(5)	0.0034(6)	0.0043(5)
O4	0.0112(7)	0.0136(7)	0.0079(7)	0.0022(5)	0.0030(6)	0.0067(6)
O5	0.0092(6)	0.0116(7)	0.0088(7)	0.0018(5)	0.0037(6)	0.0046(5)
O6	0.0083(6)	0.0090(7)	0.0089(7)	0.0015(5)	0.0038(6)	0.0030(5)
O7	0.0075(6)	0.0102(7)	0.0097(7)	0.0007(5)	0.0033(6)	0.0024(5)
O8	0.0094(6)	0.0083(7)	0.0095(7)	0.0023(5)	0.0040(6)	0.0036(5)
O9	0.0130(7)	0.0091(7)	0.0117(7)	0.0037(6)	0.0025(6)	0.0031(6)
O10	0.0079(7)	0.0209(8)	0.0160(8)	0.0013(6)	0.0061(6)	0.0015(6)
O11	0.0083(6)	0.0129(7)	0.0090(7)	0.0036(5)	0.0042(6)	0.0045(5)
O12	0.0126(7)	0.0110(7)	0.0107(7)	0.0047(5)	0.0064(6)	0.0067(6)
O13	0.0087(7)	0.0100(7)	0.0116(7)	0.0030(5)	0.0030(6)	0.0032(5)
O14	0.0098(7)	0.0167(8)	0.0096(7)	0.0025(6)	0.0044(6)	0.0056(6)
O15	0.0140(7)	0.0126(7)	0.0153(8)	0.0028(6)	0.0081(6)	0.0063(6)
O16	0.0092(6)	0.0094(7)	0.0091(7)	0.0020(5)	0.0033(6)	0.0036(5)
O17	0.0107(7)	0.0215(8)	0.0193(9)	0.0122(7)	0.0097(7)	0.0076(6)
O18	0.0087(6)	0.0092(7)	0.0090(7)	0.0017(5)	0.0028(6)	0.0034(5)
O19	0.0085(7)	0.0182(8)	0.0148(8)	0.0069(6)	0.0056(6)	0.0047(6)
O20	0.0145(7)	0.0071(7)	0.0106(7)	0.0015(5)	0.0066(6)	0.0029(5)
O21	0.0278(8)	0.0092(7)	0.0111(8)	0.0023(6)	0.0087(7)	0.0072(6)
O22	0.0116(7)	0.0103(7)	0.0122(7)	0.0046(6)	0.0022(6)	0.0038(6)
O23	0.0161(8)	0.0144(8)	0.0321(10)	0.0036(7)	0.0147(8)	0.0057(6)
O24	0.0095(6)	0.0100(7)	0.0124(7)	0.0014(6)	0.0052(6)	0.0038(5)
O25	0.0102(7)	0.0102(7)	0.0099(7)	0.0024(5)	0.0043(6)	0.0042(5)
O26	0.0090(7)	0.0129(7)	0.0170(8)	−0.0003(6)	0.0065(6)	0.0020(6)
O27	0.0079(6)	0.0109(7)	0.0106(7)	0.0021(6)	0.0033(6)	0.0032(5)
O28	0.0175(7)	0.0110(7)	0.0104(7)	0.0019(6)	0.0021(6)	0.0073(6)

mean planes of the layers are given in Figures 2(b) and (c). Within layer I, twelve octahedral wide bands parallel to [010] can be identified. Linkage between the octahedra is provided by edge-sharing. The tetrahedra and octahedra of layer II (Figure 2(b)) share common corners. In more detail, this sheet can be subdivided into (i) *vierer* single chains of tetrahedra and (ii) ribbons containing octahedra and tetrahedra in the ratio 1:2. Again, both one-dimensional elements are running parallel to the *b*-axis. As can be seen from Figure 2(a), the “free” vertices of all tetrahedra in a specific chain

point into the same direction, *i.e.*, the sequence of directedness is either up or down. The fundamental units of the mixed-polyhedral bands are MT_2O_{12} clusters, where the MO_6 moieties, share *trans*-vertices with the adjacent two tetrahedral groups. It is this group that Mumme *et al.*^[4] referred to as “winged octahedra.” One of these two tetrahedra resides above the hexagonally shaped vacancy of the neighboring octahedral sheet.

Notably, there is no direct connection between adjacent bands within the same octahedral layer. The ribbons are linked by (i) the three basal oxygens of the

Table IV. Selected Bond Lengths for FCAM-I in [Å]

M1		
O4	2.3021	(0.0014)
O9	2.3097	(0.0015)
O21	2.3206	(0.0016)
O6	2.4515	(0.0014)
O12	2.5271	(0.0016)
O28	2.5262	(0.0015)
M2		
O10	2.1590	(0.0016)
O19	2.2014	(0.0015)
O24	2.2119	(0.0016)
O10	2.2289	(0.0017)
O17	2.2840	(0.0017)
O27	2.3003	(0.0014)
M3		
O2	2.2930	(0.0014)
O22	2.3197	(0.0015)
O20	2.3285	(0.0015)
O1	2.4541	(0.0014)
O25	2.5142	(0.0015)
O18	2.5121	(0.0015)
M4		
O27	1.9493	(0.0015)
O24	1.9606	(0.0015)
O5	2.0210	(0.0015)
O3	2.0208	(0.0015)
O11	2.0504	(0.0014)
O7	2.0613	(0.0014)
M5		
O1	2.0171	(0.0014)
O6	2.0317	(0.0014)
O25	2.0393	(0.0014)
O28	2.0396	(0.0014)
O8	2.0914	(0.0014)
O13	2.0915	(0.0015)
M6		
O23	2.0158	(0.0017)
O15	2.0433	(0.0016)
O17	2.0469	(0.0014)
O26	2.0826	(0.0014)
O19	2.1024	(0.0016)
O26_2	2.2150	(0.0016)
M7		
O27	1.9423	(0.0014)
O18	1.9888	(0.0013)
O1	1.9952	(0.0014)
O13	2.0487	(0.0015)
O14	2.0619	(0.0014)
O5	2.1425	(0.0015)
M8		
O28	1.9535	(0.0015)
O12	1.9862	(0.0015)
O14	2.0227	(0.0015)
O5	2.0666	(0.0014)
O8	2.0660	(0.0013)
O7	2.0782	(0.0014)
M9		
O23	1.8918	(0.0015)
O19	1.9945	(0.0016)
O24	2.0340	(0.0013)
O26	2.0382	(0.0015)
O11	2.0833	(0.0015)
O16	2.0966	(0.0015)

Table IV. continued

M10		
O25	1.9788	(0.0015)
O18	2.0018	(0.0014)
O13	2.0417	(0.0014)
O16	2.0507	(0.0015)
O3	2.0673	(0.0014)
O11	2.0921	(0.0015)
M11		
O10	1.9149	(0.0016)
O15	1.9303	(0.0014)
O17	1.9804	(0.0015)
O14	2.0595	(0.0015)
O27	2.0617	(0.0013)
O7	2.0730	(0.0015)
M12		
O24	1.9349	(0.0015)
O26	1.9847	(0.0014)
O12	1.9911	(0.0013)
O8	2.0519	(0.0015)
O16	2.0582	(0.0014)
O3	2.1272	(0.0015)
T1		
O4	1.7842	(0.0015)
O18	1.8600	(0.0014)
O11	1.8710	(0.0014)
O5	1.8723	(0.0015)
T2		
O2	1.7813	(0.0015)
O12	1.8616	(0.0014)
O3	1.8681	(0.0014)
O7	1.8724	(0.0014)
T3		
O23	1.8927	(0.0018)
O28	1.9426	(0.0016)
O13	1.9722	(0.0015)
O14	1.9849	(0.0015)
T4		
O20	1.7471	(0.0014)
O9	1.7525	(0.0016)
O6	1.7956	(0.0015)
O26	1.7977	(0.0015)
T5		
O15	1.8483	(0.0015)
O25	1.9058	(0.0014)
O8	1.9385	(0.0015)
O16	1.9425	(0.0014)
T6		
O9	1.7294	(0.0015)
O21	1.7294	(0.0015)
O17	1.7748	(0.0015)
O1	1.7815	(0.0015)
T7		
O22	1.7338	(0.0015)
O4	1.7404	(0.0015)
O20	1.7466	(0.0015)
O19	1.7570	(0.0015)
T8		
O21	1.7180	(0.0015)
O22	1.7216	(0.0015)
O10	1.7347	(0.0015)
O2	1.7344	(0.0015)

Fig. 2—(a) Projection of the whole crystal structure of FCAM-I parallel to (20-1). Fundamental layers I (b) and II (c) are given in projections perpendicular to (20-1). For details, see text.

tetrahedral chains located directly above and below, respectively, and (ii) the octahedra of the MT₂O₁₂ clusters (by sharing common edges).

As mentioned above, the assignment of different chemical species to individual sites was performed by the program OccQP^[18] using the chemical composition obtained by EMPA (corresponding to Ca_{2.90}Mg_{0.95}Fe_{10.11}Al_{5.99}O₂₈) and the results of the structure refinement as input. Based on a quadratic approach, the program is able to assign occupancies at multiply occupied atom positions (Figure 3) in a structure.^[18] Accordingly, nine of the twelve octahedral sites are preferentially occupied by Fe³⁺, (M4-M12), while calcium is predominantly located on the remaining three positions (M1 to M3). Moreover, the results indicate that the pure calcium positions M1 and M3 are located at the outer rims of the octahedral bands (see Figure 2(c)). The M2 site, in turn, occupying the center of the ribbons contains a larger amount of calcium cations but also magnesium and iron ions. Furthermore, it is the only position where the presence of a significant

quantity of vacancies was suggested. Notably, in SFCA-I this site has been assigned to be fully occupied with Ca.

Most of the symmetrically independent TO₄ groups show a clear preference for a specific cation type. Al³⁺ ions, for example, are preferentially located on the four tetrahedra (T4, T6, T7, T8) comprising the tetrahedral chains. Two of the tetrahedra, T3 and T5 belonging to the winged octahedra show a definite enrichment in iron, whereas the cation distribution on the remaining two tetrahedral sites (T1,T2) is more flexible. It is worth noting that the suggested cation distribution shows no clear preference of magnesium for a specific site. The single magnesium atom per formula unit is structurally distributed among several sites including tetrahedral and octahedral coordination environments. However, no magnesium incorporation could be detected on the tetrahedra forming the chains (Figure 3).

Based on results of the single-crystal structure analysis, the powder pattern of the polycrystalline material was studied by a LeBail fit^[20] (see Figure 4) indicating

Fig. 3—Optimized site populations obtained from the application of the program OccQP (Color figure online).

Fig. 4—Comparison between the observed X-ray powder diffraction pattern (blue) of the 1473.15 K (1200 °C) experiment and a LeBail fit (red) corresponding to the unit cell parameters obtained from the single crystals of FCAM-I. Tick marks for the Bragg peaks are also indicated. The gray line represents the difference curve between observed and calculated step intensities (Color figure online).

that the materials obtained from the solid-state reactions at 1473.15 K (1200 °C) and the single-crystal growth experiments are equivalent. Moreover, no obvious unexplained peaks remained, strongly suggesting that FCAM-I has been synthesized in phase pure form.

B. Stability Relations of FCAM-I

1. XRPD Measurements (Experiments in Air)

The phase evolution as a function of temperature was followed by a series of powder diffraction patterns, which were collected *ex situ* after quenching the samples from the respective maximum reaction temperature (see Figure 5). According to these measurements, FCAM-I seems to be stable up to a temperature of about

1573.15 K (1300 °C). Differences in relative intensities and peak positions between the patterns acquired for the samples prepared at 1473.15 K and 1573.15 K (1200 °C and 1300 °C) are not very pronounced and may be due to slightly different cation distributions on the various sites. The diffractogram for the 1673.15 K (1400 °C) sample, however, reveals drastic changes involving shifts of reflections as well as appearing of new and disappearing of already existing peaks. Three regions (at about 8, 35, and 57 deg 2 θ) where these effects are especially obvious have been highlighted in Figure 5. Notably, the new isolated low-angle peaks at about 6.6 and 9.5 deg 2 θ cannot be explained with unit cell metric of FCAM-I. There are at least two possible explanations for these observations: (i) a disintegration of FCAM-I

Fig. 5—Powder XRD patterns of samples from selected synthesis experiments 1473.15 K, 1573.15 K, 1673.15 K, and 1698.15 K (1200 °C, 1300 °C, 1400 °C, and 1425 °C) showing a shift of selected peak positions and a decrease in their intensities with increasing temperature. This compares well with the EMPA data and the change in the chemical composition of FCAM-I. At 1673.15 K and 1698.15 K (1400 °C and 1425 °C), the XRD diagrams at low 2θ angles confirm the presence of a newly formed phase.

into an assemblage of new phases or (ii) a phase transition of FCAM-I into a new high-temperature polymorph. At slightly higher temperatures (1698.15 K (1425 °C)), the reaction seems to be complete, *i.e.*, the characteristic reflections of FCAM-I are barely visible.

2. TGA: DTA Results

In addition, the thermal behavior of FCAM-I was investigated using TGA analysis under a controlled gas flow of air. Notably, after decarbonization of the starting composition between 873.15 K and 1043.15 K (600 °C and 770 °C), no clear exothermic peak is visible (Figure 6). However, the curve increases to a maximum at 1466.15 K (1193 °C). In contrast, the experiment in He atmosphere reveals a slightly more pronounced exothermic maximum in nearly the same temperature region (1441.15 K (1168 °C)). Under oxygen atmosphere, the exothermic maximum is shifted to slightly

higher temperatures and can be located at 1485.15 K (1212 °C).

After 1466.15 K (1193 °C), the synthesis in air provides strong evidence for the stable occurrence of FCAM-I since the heat flow shows a constant negative or more precisely an endothermic gradient with a significant change in the slope at 1588.15 K (1315 °C). Contemporaneously above 1573.15 K (1300 °C), the TGA curve shows a gradual loss of mass. By heating the sample above 1685.15 K (1412 °C), a small exothermic maximum followed by melting accompanied with a significant weight loss at 1713.15 K (1440 °C) can be observed. In analogy, the curve measured in He gas has a similar shape with a substantial shift of the melting point to lower temperatures down to 1646.15 K (1373 °C). There is no significant exothermic maximum during the melting process in the O₂ atmosphere, but it can be determined by the DTA curve during cooling.

Fig. 6—Differential thermal and thermogravimetric analysis of the FCAM-I starting mixture heated by 5 K/min in air, He, and O₂ atmosphere.

The mass loss due to the reduction of Fe₂O₃ to FeO and into pure iron occurs at lower temperatures of 1310.15 K (1037 °C).

The TG-DTA results in controlled O₂ atmosphere clearly show similarities with the experiments in air. The formation of melt at 1727.15 K (1454 °C) occurs later and simultaneously the loss of mass accompanying the reaction of hematite to magnetite is negligible when compared with the other two experiments.

The synthesis experiments in the furnaces clearly correspond to the TG-DTA experiments in air. FCAM-I was not observed in the synthesis experiments below 1473.15 K (1200 °C). The synthesis experiments also disclosed that iron(III)oxide starts to be reduced to iron(II)oxide at temperatures between 1573.15 K and 1673.15 K (1300 °C and 1400 °C). Concurrently, at 1573.15 K (1300 °C) the FCAM-I phase breaks down forming a complex assemblage of new phases. Finally, the FCAM-I phase disappears completely at temperatures above 1673.15 K (1400 °C).

3. EMPA Results

Electron microprobe analysis clearly supports the previous results. Evaluation of the samples using backscatter electron (BSE) images yields the typical polycrystalline granular microstructure in the 1473.15 K

(1200 °C) experiment (Figure 7(d)). After 24 hours, the crystallite size is 10 to 20 μm. The size increases from 10 μm in the 1473.15 K (1200 °C) experiments to about 100 μm in the highest temperature experiments performed at 1673.15 K (1400 °C). Exceeding 1673.15 K (1400 °C) melt dominates in the samples and the FCAM-I phase disintegrates completely. Chemical analysis confirms a homogenous composition of FCAM-I phases below 1573.15 K (1300 °C) which corresponds with the stoichiometric end-member composition. Increasing temperatures lead to a reduction of Fe³⁺ to Fe²⁺ in FCAM-I (Figure 8; Table V). This is also accompanied by a decrease in the calcium content in FCAM-I and the formation of new calcium-rich Fe-Al-oxide phases. These new phases are solid solutions between calcium aluminates and calcium ferrites. During this reaction, the aluminum contents increase (Figure 9). The calculated Fe²⁺ concentrations of FCAM-I increase from 0 atoms per formula unit (apfu) up to 0.59 apfu. The concentration of calcium decreases considerably from 3.08 apfu down to 1.79 apfu (FCAM-I → FCAM-I^{low}). Consequently, an increase in magnesium in the FCAM-I phase occurs. At 1573.15 K (1300 °C), FCAM-I starts to break down and reaction textures occur (Figure 7(e)), which can be explained with the following model Reaction (1).

Fig. 7—BSE images of the experimental series with samples prepared at 1573.15 K, 1623.15 K, and 1673.15 K (1300 °C, 1350 °C, and 1400 °C) using the platinum double-capsule technique with a controlled oxygen fugacity *via* the hematite-magnetite buffer (*a* and *c*). (*a*) Illustrates the newly formed SFCA-I in a matrix of unreacted starting material. The disintegration of the polycrystalline FCAM-I phases starts at 1623.15 K (1350 °C) (*b*) and the formation of $\text{MA}_{0.37}\text{F}_{0.625}$ at temperatures above 1673.15 K (1400 °C) (*c*). For comparison, the BSE image of the 1473.15 K, 1573.15 K, and 1673.15 K (1200 °C, 1300 °C, and 1400 °C) experiments in air are shown in *d* through *f*. The first BSE image shows fine-grained, polycrystalline FCAM-I phases synthesized at 1473.15 K (1200 °C) in air (*d*). Disintegration of FCAM-I with a typical crystallite size of 10 to 20 μm starts at 1573.15 K (1300 °C). Simultaneously significant crystal growth of FCAM-I can be observed. The newly formed phases are shown in (*e*). The last BSE image (*f*) shows the 1673.15 K (1400 °C) experiment. The main phases in the sample are quenched materials, which are mostly solid solutions of $\text{C}_2\text{A}_{0.25}\text{F}_{0.75}$ and $\text{CA}_{0.75}\text{F}_{1.25}$. Also clearly visible is the disintegration of FCAM-I and the new formation of $\text{MA}_{0.37}\text{F}_{0.625}$.

For comparison, the formation of FCAM-I in the platinum double-capsule technique with a controlled oxygen fugacity *via* the hematite-magnetite buffer begins at higher temperatures. Hence, the stability field of FCAM-I shifts to significantly higher temperatures. In the first experiment at 1473.15 K (1200 °C), no significant reaction occurs in the starting mixture. The BSE image (Figure 7(a)) and the EMPA analysis of the 1573.15 K (1300 °C) experiment show the formation of FCAM-I in a finely granulated matrix of the initial starting mixture. FCAM-I forms crystals with a size of ca. 100 μm. In contrast to the experiments in air, the FCAM-I phase is stable up to 1573.15 K (1300 °C). After heating the sample by another 50 K, the first breakdown textures of FCAM-I can be observed (Figure 7(b)). Equivalent to the experiments in air increasing the temperature leads to a decrease of the calcium content of FCAM-I. However, the positive shift of the aluminum content starts only after this heating step. At temperatures above 1673.15 K (1400 °C), the FCAM-I phase shows a significant increase of Al concentration from 6.08 to 6.92 apfu. The calculated Fe^{2+} content of the FCAM-I phase in this series is around 0.40 and 0.56 apfu.

The first quenched materials in the intergranular space have a chemical composition in the system CF-CA with the actual composition of $\text{Ca}_{1.10}\text{Fe}_{1.32}\text{Al}_{0.65}\text{O}_4$ ($\text{CA}_{0.25}\text{F}_{0.75}$). Between FCAM-I and the intergranular spaces are small quenched phases which exhibit a typical needle-like habitus. The chemical analyses correspond to

the system of the so-called $\text{CF}_3\text{-CA}_3$ phases with the exact composition of $\text{Ca}_{1.05}\text{Al}_{1.95}\text{Fe}_{4.00}\text{O}_{10}$ or CAF_2 . In both phases, the calculated Fe^{2+} concentration is zero. The phases $\text{CA}_{0.25}\text{F}_{0.75}$ and CAF_2 were detected at 1573.15 K (1300 °C) in air and in the platinum capsule experiment at 1623.15 K (1350 °C) (Figures 7(b) and (e)).

The synthesis in air proves that with increasing temperature the phase in the intergranular space changes the composition from $\text{Ca}_{1.10}\text{Fe}_{1.32}\text{Al}_{0.65}\text{O}_4$ to $\text{Ca}_{1.97}\text{Al}_{0.58}\text{Fe}_{1.52}\text{O}_5$ corresponding to a solid solution between the phases C_2F and C_2A with calculated Fe^{2+} contents of 0.05 apfu. The formation of iron (II) shows a change in the $f\text{O}_2$ environment from oxidizing conditions at 1573.15 K (1300 °C) to slightly reducing settings at 1673.15 K (1400 °C) as indicated by model Reaction (2). Nevertheless, EMPA of the 1673.15 K (1400 °C) experiments confirm the presence of the $\text{CF}_2\text{-CA}_2$ phase with a composition of $\text{Mg}_{0.01}\text{Ca}_{0.94}\text{Al}_{1.25}\text{Fe}_{2.80}\text{O}_7$ or simplified $\text{CaAlFe}_3\text{O}_7$ ($\text{CA}_{0.75}\text{F}_{1.25}$). The phase shows a similar needle-like habitus like the CAF_2 phase.

Fig. 8—Plot of Fe^{2+} content [apfu] in FCAM-I vs temperatures.

The textures in the BSE image of Figure 7(f) clearly demonstrate the breakdown of FCAM-I to CAF_2 and $\text{CA}_{0.75}\text{F}_{1.25}$. The calculated Fe^{2+} content in the $\text{CA}_{0.75}\text{F}_{1.25}$ phase is about 0.11 apfu.

The two phases $\text{C}_2\text{A}_{0.25}\text{F}_{0.75}$ and $\text{CA}_{0.75}\text{F}_{1.25}$ could not be detected in the experimental series under controlled oxygen fugacity. At temperatures exceeding 1673.15 K (1400 °C) but prior to melting, the complete breakdown of FCAM-I to a newly formed phase ($\text{MA}_{0.375}\text{F}_{0.625}$) occurs (Figure 7(f)) as indicated by model Reactions (3) and (4). The calculated chemical composition based on 8 oxygens and 6 cations corresponds to $\text{Mg}_{0.51}\text{Ca}_{0.04}\text{Fe}_{0.45}^{2+}\text{Fe}_{1.16}^{3+}\text{Al}_{0.84}\text{O}_4$ or $(\text{Mg}, \text{Fe}^{2+})(\text{Al}, \text{Fe}^{3+})_2\text{O}_4$. The stability field of this new spinel-type magnesium-aluminum-ferrite shows no correlation with oxygen fugacity (Figures 7(c) and (f)). In the double-capsule experiment as well as in the synthesis in air, $\text{MA}_{0.375}\text{F}_{0.625}$ can be detected at temperatures

Table V. Average Chemical Compositions of Selected FCAM-I Phases (apfu) with Calculated Fe^{2+} and Fe^{3+} Content as a Function of Increasing Temperatures

	T [K]	T [°C]	Mg	Al	Ca	Fe^{3+}	Fe^{2+}	Σ Cations	O
FCAM-I	1473.15	1200	1.01	5.94	3.05	10.00	0.00	20.00	28.00
	1573.15	1300	1.30	6.41	2.42	9.59	0.28	20.00	28.00
	1623.15	1350	1.59	7.04	1.90	8.96	0.51	20.00	28.00
FCAM-I ^(low)	1673.15	1400	1.63	7.26	1.81	8.74	0.56	20.00	28.00

above 1673.15 K (1400 °C). It is chemically very homogenous and exhibits only a very small standard deviation of ± 0.01 apfu in magnesium, aluminum, and iron. The calculated Fe^{2+} content is about 0.90 apfu.

IV. DISCUSSION

FCAM-I can be synthesized at temperatures above 1463.15 K (1190 °C) in air. This phase breaks down

Fig. 9—The Fe_2O_3 - CaO - Al_2O_3 (FCA) triangle (a) illustrates the starting composition and the chemical variation of FCAM-I phases as a function of temperature.^[21] Also plotted (b) are the different quench phases observed in the samples which have been heated above 1573.15 K (1300 °C).

(Figure 7) in two steps: at 1583.15 K (1310 °C) due to the release of Ca, Fe, Al ($\text{FCAM-I} \rightarrow \text{FCAM-I}^{\text{low}}$) and the formation of new calcium-aluminum-ferrites ($\text{CA}_{0.25}\text{F}_{0.75}$ and CAF_2). In the second step, at temperatures above 1683.15 K (1410 °C) FCAM-I disappears completely by forming magnesium-aluminum-ferrites (MF-MA) and subsequently melt. The growth of CAF_2 and $\text{MA}_{0.375}\text{F}_{0.25}$ is predominantly a function of increasing temperatures. In contrast, increasing the oxygen fugacity leads to a positive correlation with the stability field of FCAM-I and hence the $f\text{O}_2$ concentration has a significant influence on the nature of the newly formed components. Reducing conditions (decreasing O_2 fugacity) favor the reduction of Fe^{3+} to Fe^{2+} and the formation of the phases C_2F - C_2A ($\text{C}_2\text{A}_{0.25}\text{F}_{0.75}$) as well as CF_2 - CA_2 ($\text{CA}_{0.75}\text{F}_{1.25}$).

The EMP analyses in conjunction with the textures observed in the BSE images clearly demonstrate that the calcium content in FCAM-I decreases with increasing temperature and simultaneously new calcium-rich phases appear. This suggests that FCMA-I still remains stable up to higher temperatures by simply adjusting its composition with respect to Ca and Al. Bond distance calculations indicate that the M_2O_6 polyhedron located in the center of the fundamental bands of layer-type I (Figure 2(a)) is significantly smaller (Table IV) compared to the octahedral sites around M1 and M3 ($\langle \text{M-O} \rangle \sim 2.23$ vs ~ 2.41 Å, respectively). On the other hand, site occupancy analysis indicates that the M_2O_6 octahedron shows a mixed cation population, whereas the octahedra M1 and M3 are almost exclusively occupied by calcium cations, indicating that the incorporation of calcium on M2 is the limiting factor for the incorporation of Ca^{2+} into the FCAM-I structure. Hence at higher temperatures, FCAM-I has presumably an ideal total calcium content of 2 calcium apfu that favors the stability of the structure (see Table VI).

Comparing the investigations using TG-DTA data acquired under different atmospheres demonstrates that the stability field of FCAM-I is mostly controlled by the concentration of Fe^{2+} . Compared to the experiments in air, higher oxygen fugacity expands the stability field of

Table VI. Representative Electron Microprobe Analysis and Formula Stoichiometry of the Experimentally Obtained Phases

Symbol	Formula	Fe ₂ O ₃ + FeO [weight percent]	CaO [weight percent]	Al ₂ O ₃ [weight percent]	MgO [weight percent]	Σ [weight percent]	Ca [apfu]	Mg [apfu]	Al [apfu]	Fe ³⁺ [apfu]	Fe ²⁺ [apfu] ^a	O [apfu]
FCAM-I	Ca ₃ MgAl ₆ Fe ₁₀ O ₂₈	60.68	12.87	23.05	03.39	100.00	3.01	1.10	5.94	9.98	—	28.00
CAF ₂	CaAl ₂ Fe ₄ O ₁₀	66.68	12.38	20.88	00.54	100.48	1.06	0.06	1.95	3.97	—	10.00
CA _{0.25} F _{0.75}	CaAl _{0.5} Fe _{1.5} O ₄	51.59	32.91	15.20	00.13	99.83	1.17	—	0.60	1.28	—	4.00
C ₂ A _{0.25} F _{0.75}	Ca ₂ Al _{0.5} Fe _{1.5} O ₅	46.98	42.77	09.79	—	99.54	1.97	—	0.49	1.50	0.04	5.00
CA _{0.75} F _{1.25}	CaAl _{1.5} Fe _{2.5} O ₇	65.18	12.65	20.38	02.02	100.23	0.85	0.04	1.35	2.65	0.11	7.00
MA _{0.375} F _{0.625}	(Mg, Fe ²⁺)Fe _{1.25} ³⁺ Al _{0.75} O ₄	66.90	01.19	23.13	11.04	102.26	0.04	0.51	0.84	1.16	0.45	4.00
FCAM-I ^{low}	Ca ₂ Mg ₂ Al ₇ Fe ₉ O ₂₈	59.15	08.03	29.26	05.28	101.72	1.79	1.65	7.20	8.79	0.57	28.00

^aCalculated.

FCAM-I of only about 30 K to higher temperatures Table VI.

Under atmospheric conditions in which the formation of Fe²⁺ is favored, the breakdown of FCAM-I shifts to a significantly lower temperature from 1683.15 K (1410 °C) down to 1622.15 (1349 °C) in He atmosphere—and concurrently the stability field of FCAM-I decreases noticeably.

It appears that with the increasing Fe²⁺ concentration in FCAM-I the charge balance can be maintained by the release of Ca²⁺. This observation is based on the increase of Fe²⁺ (≥ 0.6 apfu) and a simultaneous release of calcium from the M₂O₆ octahedra. Additional deficit of Ca on the octahedra around M1 and M3 ($\ll 1.8$ apfu) then ultimately leads to the breakdown of the FCAM-I structure.

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REFERENCES

1. J. Hancart, V. Leroy, A. Bragard: *CNRM Metall*, 1967, Report, pp. 3–7.
2. W. Mumme: *N. Jb. Miner. Mh.*, 1988, pp. 359–66.
3. J. Hamilton, B. Hoskins, W. Mumme, and W. Borbidge: *Neues Jb. Miner-Abh.*, 1989, vol. 161 (1), pp. 1–26.
4. W. Mumme, J. Clout, R. Gable: *Neues Jb. Miner-Abh.*, 1998, pp. 93–117.
5. W. Mumme: *Neues Jb. Miner-Abh.*, 2003, vol. 178 (3), pp. 307–35.
6. N.A. Webster, M.I. Pownceby, I.C. Madsen, and J.A. Kimpton: *Metall. Mater. Trans. B*, 2012, vol. 43B (6), pp. 1344–57.
7. T.R. Patrick and M.I. Pownceby: *Metall. Mater. Trans. B*, 2002, vol. 33B (1), pp. 79–89.
8. M. Kalenga and A.M. Garbers-Craig: *J. S. Afr. Inst. Min. Metall.*, 2010, vol. 110 (8), p. 447.
9. Bruker-AXS: *TOPAS version 4.2—software for powder diffraction data*, 2009, Karlsruhe, Germany.
10. R.A. Robie, B.S. Hemingway: *US Geol. Surv—Info. Ser.*, 1995, 1–5, pp. 192–93.
11. ICDD PDF-4+ Version 4: *1302 International Centre for Diffraction Data Powder Diffraction File*, Newtown Square Pennsylvania, 2013.
12. R.W. Cheary and A. Coelho: *J. Appl. Crystallogr.*, 1992, vol. 25 (2), pp. 109–21.
13. Program CrysAlis: Agilent Technologies, Yarnton, England, 2014.
14. E. Prince, A.J.C. Wilson: *Int. Tables Crystallogr.*, 2004, vol. C.
15. M.C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G.L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, and R. Spagna: *J. Appl. Crystallogr.*, 2005, vol. 38 (2), pp. 381–88.
16. G.M. Sheldrick: *Acta Crystallogr Sect A*, 2008, vol. 64 (1), pp. 112–22.
17. L.J. Farrugia: *J. Appl. Crystallogr.*, 1999, vol. 32 (4), pp. 837–38.
18. S.E. Wright, J.A. Foley, J.M. Hughes, S.E. Wright, J.A. Foley, and J.M. Hughes: *Am. Mineral.*, 2000, vol. 85 (3–4), pp. 524–31.
19. E. Dowty: *ATOMS6. 4—Shape Software*, Kingsport, USA, 2011.
20. A. Le Bail: *Powder Diff.*, 2005, vol. 20 (04), pp. 316–26.
21. R. Dayal, F. Glasser: *Science of Ceramics*, Academic Press, London, 1967, pp. 191–214.