

The Al-Rich Part of the System CaO–Al₂O₃–MgO

Part I. Phase Relationships

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In the Al-rich part of the ternary system CaO–Al₂O₃–MgO two new ternary phases Ca₂Mg₂Al₂₈O₄₆ (CAM-I) and CaMg₂Al₁₆O₂₇ (CAM-II) with limited solid solution ranges were found. Due to the fact that the compositions of the Mg-rich end members of these solid solutions lie on the join between hibonite (CaAl₁₂O₁₉) and spinel (MgAl₂O₄), the model of the crystal structures of these phases can be constructed by a suitable combination of hibonite and spinel units. Both phases, CAM-I and CAM-II, exhibit solid solution ranges described by a substitution mechanism also found in the binary spinel phase, MgAl₂O₄: 3 Mg²⁺ = 2 Al³⁺ + □. Thus the ternary phases can be expressed by the chemical formulas. Ca₂Mg_{2-3x}Al_{28+2x}□_xO₄₆ for CAM-I with 0 ≤ x ≤ 0.30 and CaMg_{2-3y}Al_{16+2y}□_yO₂₇ for CAM-II with 0 ≤ y ≤ 0.2. © 1995 Academic Press, Inc.

INTRODUCTION

The thermodynamics of the system CaO–Al₂O₃ was studied by Kumar and Kay (1) by means of the EMF-method applying a Ca–aluminate solid state electrolyte which they claimed to be β-alumina phase. It is to be assumed that a universal application of a cation conductor of this or of any comparable kind will open many important paths in thermodynamic experimentation. Thus it is the aim of the present work to study the stable phase relationships in the Al-rich section of the system CaO–Al₂O₃ and its extension into the system CaO–Al₂O₃–MgO.

Among the approved cation conducting solid state electrolytes a considerable amount of research was focused on the group of β-aluminas. Concentrating on Na–β-alumina, NaAl₁₁O₁₇, preparation techniques for dense sintered samples, crystal structures, and some phase relationships have been studied (2–10). According to Moseley (6) different β-alumina phases have been synthesized which contain Li₂O or MgO in addition to Na₂O and Al₂O₃ resulting in slight modifications of the crystal structure.

The cation exchange of Na by other elements has been reported (11–13) to allow the production of the corre-

sponding β-aluminas for instance Ca–β-alumina. According to Kirchnerova *et al.* (12) Ca–β-aluminas can only be obtained from Na–β-aluminas by such ion exchange processes in a suitable salt melt, while a direct synthesis is not possible. There is an agreement among these authors, however, that Ca–β-aluminas are metastable.

Kumar and Kay (1), Hong *et al.* (14), and Schäfer *et al.* (15), on the other hand, have reported the direct syntheses of Ca–β-aluminas at high temperatures (1650°C) starting with appropriate mixtures of oxides and carbonates. Recently, however, Fray and Kumar (16) claimed that the solid state electrolyte used by Kumar and Kay (1) was not a β-alumina but rather had a magnetoplumbite structure.

Products prepared by ion exchange from Na–β-alumina and by direct high-temperature synthesis are different, however, as revealed by a comparison of X-ray powder patterns presented by Kirchnerova *et al.* (12) and by Kumar and Kay (1).

In our own preliminary experiments, starting with a commercial Na–β-alumina pellet, a Ca-ion exchange process was performed, following the experimental procedure suggested by Kirchnerova *et al.* (12). The product formed showed an X-ray powder pattern corresponding to that presented by Kirchnerova *et al.* for Ca–β-alumina. A subsequent heating experiment at temperatures above 1650°C resulted in a decomposition of the Ca–β-alumina and the formation of an assemblage consisting essentially of a magnetoplumbite-phase. It is thus concluded that the Ca–β-alumina is metastable while the phase with magnetoplumbite structure is stable. In the present paper only stable high-temperature phase assemblages will be investigated.

PREVIOUS WORK

A summary of previous investigations on the system CaO–Al₂O₃ is given by Nurse *et al.* (17). In the Al-rich part the phases CaAl₂O₄ (CA), CaAl₄O₇ (CA₂), and CaAl₁₂O₁₉ (CA₆) are stable, all being characterized by incongruent

melting behavior. Eriksson and Pelton (18) present a calculated phase diagram of the system CaO–Al₂O₃ based on the available thermodynamic and phase-equilibrium data. Their diagram shows an incongruent melting behavior for CaAl₁₂O₁₉ while CaAl₄O₇ and CaAl₂O₄ melt congruently.

The binary phase Ca–hexaaluminate, CaAl₁₂O₁₉, is also found as the natural meteorite mineral hibonite.

In the system MgO–Al₂O₃ the spinel MgAl₂O₄ is the only binary phase. The part MgO–MgAl₂O₄ has been studied by Alper *et al.* (20) and the part MgAl₂O₄–Al₂O₃ by Osborn (21) and Viertel and Seifert (22). At high temperatures the spinel is capable of forming wide solid solution ranges with either excess MgO or with excess Al₂O₃.

The ternary system CaO–Al₂O₃–MgO has been studied by Welch (23), by Majumdar (24), and by Glasser and Marr (25). The Al-rich part of the resulting phase diagram does not show any ternary compound.

EXPERIMENTAL METHODS

In order to determine the phase equilibria of the system CaO–Al₂O₃–MgO appropriate samples were prepared by conventional methods. Calculated batches were weighed from high purity reagents, CaCO₃, MgO, and Al₂O₃, homogenized in agate mortars under acetone, heated to 1100°C, and again milled in a tungsten carbide ball mill. Finally, small samples of the starting mixtures were equilibrated at temperatures in the range from 1400–1850°C in a vertical molybdenum-wound tube furnace controlled by a commercial Eurotherm electronic temperature controller. Depending on the temperature and the presence or absence of a melt equilibration periods ranging from 2 to 48 hr were selected.

The temperature was measured up to 1600°C by using a Pt/Pt₉₀Rh₁₀ thermocouple and at temperatures up to 1850°C by using a Pt₈₀Rh₂₀/Pt₆₀Rh₄₀ thermocouple. Calibrations were performed against the melting points of diopside (CaMgSi₂O₆) at 1393.5°C, pseudowollastonite (CaSiO₃) at 1546°C, platinum at 1772°C, and the formation of two immiscible liquids in the mixture 93 mole% SiO₂ 7 mole% CaO (26) at the invariant temperature of 1710°C. All temperatures correspond to the IPTS-68 temperature scale.

The experiments were performed in air. Quenching in water was avoided because of possible reactions. Instead, the samples were quenched by dropping them on a thick brass block with a high heat capacity.

The quench products were polished and investigated by reflected light microscopy. In many cases the reflectivities of the coexisting phases were quite similar. Thus, it was difficult to distinguish them optically.

All samples were studied by electron probe microanalysis (EPMA) on Cameca Camebax equipment using the ZAF evaluation program. On the backscattered electron

image of the samples it was possible to distinguish between the different phases and to select grains of sufficient size. The measurements were taken from grains in mutual contact. A series of measurements was performed in each sample. Only analyses with a total within the range 100 ± 2% were taken into consideration.

The products of selected samples were investigated by X-ray diffractometry. The powder patterns were obtained on a Philips PW1820 diffractometer with CuK α radiation. Si was employed as an external standard.

EXPERIMENTAL RESULTS

The Hibonite Phase in the System CaO–Al₂O₃

Schmid and de Jonge (27) investigated the Al-rich part of the system CaO–Al₂O₃ in nonequilibrium experiments. According to their results hibonite has a rather wide solid solution range due to planar structural defects.

In the present study samples equilibrated at temperatures from 1600° to 1850°C with several intermediate grindings resulted in microprobe analyses of CaAl₁₂O₁₉ deviating from stoichiometry by less than 0.4 mole% CaO. Furthermore, mixed analyses in fine grained samples containing CaAl₁₂O₁₉ coexisting either with CaAl₄O₇ or with Al₂O₃ cannot be excluded. Accordingly CaAl₁₂O₁₉ is considered to be stoichiometric.

The Al-Rich Part of the System CaO–Al₂O₃–MgO

A plot of the microprobe analyses on samples in the ternary system CaO–AlO_{1.5}–MgO revealed the existence of hibonite, CaAl₁₂O₁₉, with a limited extension into the ternary system. In addition, two new ternary phases Ca₂Mg₂Al₂₈O₄₆, CAM-I, and CaMg₂Al₁₆O₂₇, CAM-II, with rather wide ranges of solid solution were found (Fig. 1).

The Mg-rich end members of CAM-I and CAM-II plot exactly on the join between stoichiometric hibonite and spinel, MgAl₂O₄. From this fact it is concluded that these phases are constructed by a suitable combination of hibonite and spinel units.

The hibonite or magnetoplumbite structure (29, 30) contains Al₂O₃ blocks with the spinel structure of γ -Al₂O₃ intersected by Ca-bearing layers. The (111) direction of the Al-spinel block corresponds to the *c* direction of hibonite. Due to the close structural relationship between the hibonite and spinel structures mixed layer model based on an intercalation of hibonite layers and spinel layers are proposed for the ideal structures of the ternary phases. This conclusion is also supported by a similar stacking of units which has been observed by Kohn and Eckart (28) in the system BaO–FeO_{1.5}–ZnO with corresponding barium hexaferrite (BaFe₁₂O₁₉) and franklinite (ZnFe₂O₄) layers. A comparison of the stoichiometry of the phases shows

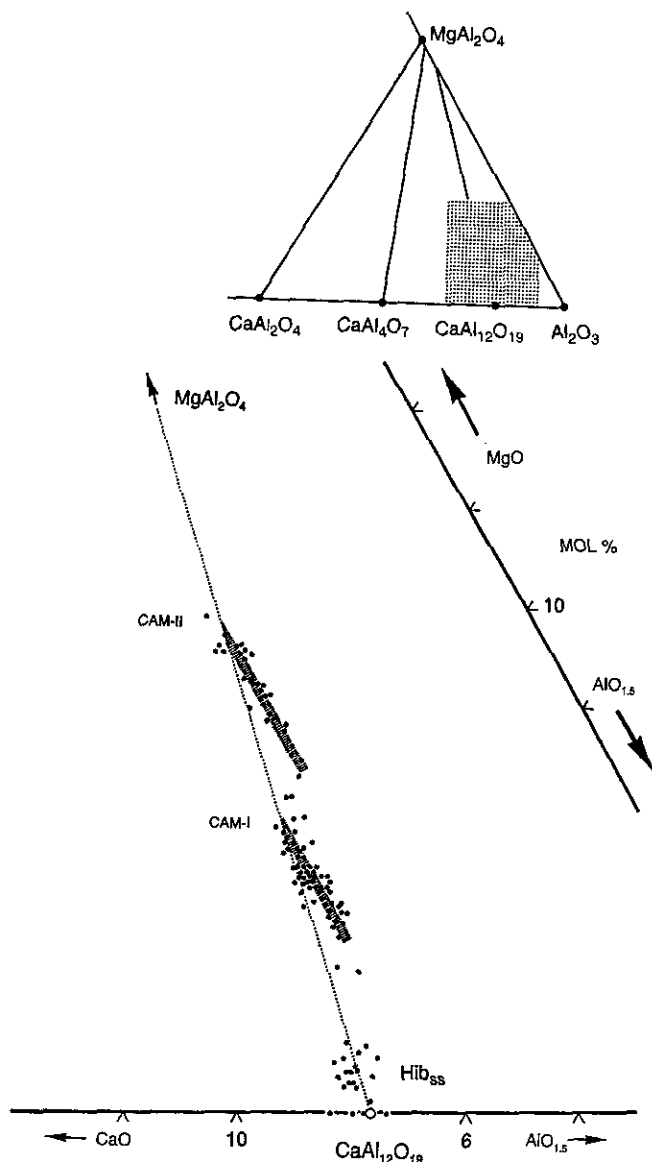
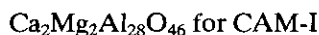
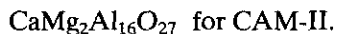


FIG. 1. EPMA data in the Al-rich part of the system CaO-AlO_{1.5}-MgO.

that CAM-I corresponds to Kohn and Eckart's "X" phase, while CAM-II corresponds to their "W" phase. The formulas of the phases are thus



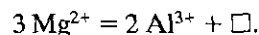
and



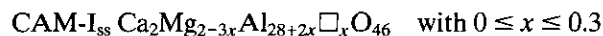
Due to the stacking of layers the corresponding *a*-cell parameter remains essentially unchanged while the *c*-cell parameters are very large.

All samples prepared for phase diagram investigations were heterogeneous showing a fine grained intergrowth of coexisting phases. Thus, in order to derive accurate X-ray powder diagrams for the phases CAM-I and CAM-II, the X-ray patterns presented in Table 1 are taken from powders from single crystals (see Part II of this paper). Even then the high cleavage parallel to the base may result in strong textural effects and correspondingly in pronounced changes of apparent relative intensities.

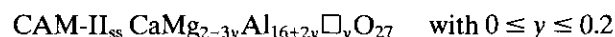
From the ideal CAM-I and CAM-II compositions solid solution series extend toward compositions with lower Mg contents. They maintain at the same time constant Ca concentrations. Their extensions parallel to the MgO-Al₂O₃ join suggest a mechanism similar to the cation exchange accepted for spinel solid solutions:



The formulas for the solid solution series following this substitution model thus are



and



The temperature dependence of the limit of the solid solution series *x* and *y* remain rather constant in the range from 1600° to 1850°C, in contrast to that of the spinel in the system MgO-Al₂O₃.

The changes of chemical composition within the solid solution ranges of CAM-I or CAM-II cannot be detected by means of X-ray powder diffractometry.

The phase relations in the system CaO-Al₂O₃-MgO at 1650°C are shown in Fig. 2. At this temperature the diagram in subsolidus throughout. The CAM-I_{ss} coexists with calciumdialuminate in Ca-excess compositions or with corundum in Ca-deficient compositions (Table 2). The CAM-II_{ss} also shows tie line relations with calciumdialuminate or on the other hand with a spinel and corundum (Table 2).

In the Ca-deficient sector CAM-II_{ss} coexists at 1800°C (Fig. 3) with a spinel phase only while CAM-I_{ss} coexists either with a spinel or with corundum (Table 2). A very narrow three-phase triangle exists between the spinel, CAM-II_{ss}, and CAM-I_{ss}. The shift of the three-phase triangle from CAM-II_{ss}-corundum-spinel at 1650°C to CAM-I_{ss}-corundum-spinel at 1800°C is evidently due to the shift of the temperature dependent composition of the spinel phase in equilibrium with corundum.

In high-CaO compositions an extended range of a liquid phase appears at 1800°C. Although the complete liquidus diagram has not yet been determined it is indicated that

TABLE 1
X-Ray Powder Patterns for CAM-I and CAM-II Taken from
Single Crystalline Material

CAM-I _{ss} Ca ₂ Mg ₂ Al ₂₈ O ₄₆ Rhombohedral <i>a</i> = 5.5710(1) <i>c</i> = 79.770(12)					CAM-II _{ss} CaMg ₂ Al ₁₆ O ₂₇ Hexagonal <i>a</i> ≈ 5.5926(2) <i>c</i> = 31.297(14)				
<i>d</i> _{obs}	<i>I</i> _{rel}	<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{obs}	<i>I</i> _{rel}	<i>h</i>	<i>k</i>	<i>l</i>
13.26	8	0	0	6	7.81	10	0	0	4
8.85	11	0	0	9	5.21	35	0	0	6
6.65	6	0	0	12	4.39	16	1	0	3
5.31	39	0	0	15	4.12	5	1	0	4
4.43	10	0	0	18	3.91	33	0	0	8
3.79	46	1	0	13	3.13	31	0	0	10
3.32	33	0	0	24	2.824	25	1	0	9
2.945	32	0	0	27	2.796	42	1	1	0
2.899	5	1	0	22	2.634	14	1	1	4
2.815	8	0	1	23	2.627	87	1	0	10
2.785	37	1	1	0	2.608	28	0	0	12
2.657	100	1	1	9	2.464	100	1	1	6
2.588	59	0	1	26	2.452	53	1	0	11
2.467	90	1	1	15	2.392	7	2	0	2
2.453	15	1	0	28	2.358	24	2	0	3
2.389	18	0	1	29	2.313	9	2	0	4
2.358	32	1	1	18	2.275	15	1	1	8
2.309	7	0	2	10	2.235	32	0	0	14
2.288	8	2	0	11	2.196	38	2	0	6
2.245	11	0	2	13	2.059	66	2	0	8
2.215	67	0	1	32	1.9872	41	2	0	9
2.171	15	0	2	16	1.9149	9	2	0	10
2.145	13	2	0	17	1.8440	6	2	0	11
2.091	18	0	2	19	1.7073	6	2	0	13
2.064	30	2	0	20	1.6198	6	2	1	9
2.045	16	0	0	39	1.6143	6	3	0	0
2.008	38	0	2	22	1.5805	46	2	0	15
1.9803	10	2	0	23	1.5646	12	0	0	20
1.9242	8	0	2	25	1.5422	21	3	0	6
1.7335	6	2	0	32	1.5392	18	2	1	11
1.6820	6	0	2	34	1.5217	38	2	0	16
1.6083	7	3	0	0	1.4657	17	2	0	17
1.5836	25	2	0	38	1.4126	13	2	0	18
1.5676	16	1	2	26	1.3982	56	2	2	0
1.5632	23	3	0	12	1.3622	20	2	0	19
1.5371	41	0	2	40	1.3144	5	2	0	20
1.5200	10	1	2	29	1.2692	5	2	0	21
1.5144	21	2	0	41	1.2345	5	3	1	10
1.4494	10	2	0	44	1.2121	6	1	0	25
1.4398	6	2	1	34	1.1179	5	0	0	28
1.3928	52	2	2	0	1.1056	5	1	1	26
1.3889	13	1	0	55					
1.3495	6	0	2	49					
1.3307	10	2	1	50					
1.2945	7	0	2	52					
1.2340	6	1	3	25					
1.2272	20	3	0	42					
1.1087	12	1	1	66					

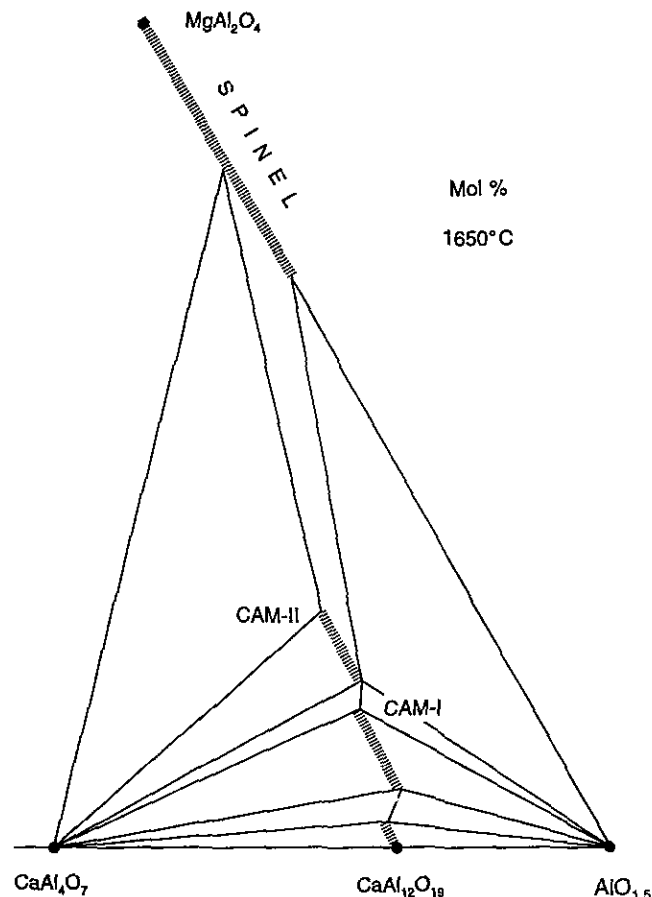


FIG. 2. Tie line relations in the Al-rich part of the system CaO-Al₂O₃-MgO at 1650°C. The system is subsolidus throughout.

both CAM-I and CAM-II melt incongruently at temperatures above 1850°C.

The compositions of the liquids coexisting with CAM-I and CAM-II were analyzed in samples quenched from 1800°C (Table 3). In order to allow the growth of single crystals of CAM-I and CAM-II (Part II of this series) mixtures corresponding to these compositions were prepared and prereacted. In analogy to an established technique (31) for growing single crystals of incongruently melting materials by the floating zone method, disks of these samples were later employed, where they formed the zone of liquid from which CAM-I and CAM-II crystals were grown.

Hibonite, CaAl₁₂O₁₉, exhibits only a limited range of ternary solid solutions in the CaO-Al₂O₃-MgO system, which is restricted, however, to MgO concentrations below 1 mole% MgO. Since hibonite contains a γ -Al₂O₃ block with vacant lattice sites a substitution model



is proposed.

TABLE 2
Phase Relations and Chemical Compositions of CAM-I_{ss} and CAM-II_{ss} Coexisting
with Spinel and Corundum at 1650 and 1800°C

Coexisting phases	CAM-I _{ss}	CAM-II _{ss}	Spinel
	$\text{Ca}_2\text{Mg}_{2-3x}\text{Al}_{28+2x}\text{O}_{46}$ $0 \leq x \leq 0.30$	$\text{CaMg}_{2-y}\text{Al}_{16+2y}\text{O}_{27}$ $0 \leq y \leq 0.20$	$\text{Mg}_{1-3z}\text{Al}_{2+2z}\text{O}_4$ $0 \leq z \leq 0.21$
1650°C			
CAM-I _{ss} + Corundum	$0 \leq x \leq 0.30$		
CAM-I _{ss} + Corundum + CAM-II _{ss}	$x = 0$	$y = 0.20$	
CAM-II _{ss} + Corundum + Spinel		$y = 0.20$	$z = 0.12$
CAM-II _{ss} + Spinel		$0 \leq y \leq 0.20$	$0.07 \leq z \leq 0.12$
1800°C			
CAM-I _{ss} + Corundum	$0 \leq x \leq 0.20$		
CAM-I _{ss} + Corundum + Spinel	$x = 0.20$		$z = 0.21$
CAM-I _{ss} + Spinel	$0.20 \leq x \leq 0.30$		$0.19 \leq z \leq 0.21$
CAM-I _{ss} + Spinel + CAM-II _{ss}	$x = 0$	$y = 0.20$	$z = 0.19$
CAM-II _{ss} + Spinel		$0 \leq y \leq 0.20$	$0.07 \leq z \leq 0.19$

CONCLUSION

In the Al-rich part of the system CaO–Al₂O₃–MgO three solid phases are stable at high temperatures above 1600°C: the well-known hibonite, CaAl₁₂O₁₉, with magnetoplumbite structure, and two magnesium bearing phases, CAM-I, Ca₂Mg₂Al₂₈O₄₆, and CAM-II, CaMg₂Al₁₆O₂₇.

Their close structural relationship, revealed by a comparison of X-ray powder patterns, and also the fact that CAM-I and CAM-II are correlated with corresponding magnetoplumbite phases X and W in the BaO–Fe₂O₃–ZnO system confirm that they all belong to the magnetoplumbite or modified magnetoplumbite structure family. A structure determination of CAM-I and CAM-II will be presented in Part II of this paper.

The addition of magnesia results in a limited incorporation into the lattice of hibonite. It is concluded that Mg is filling some of the defect cation positions in the γ -alumina

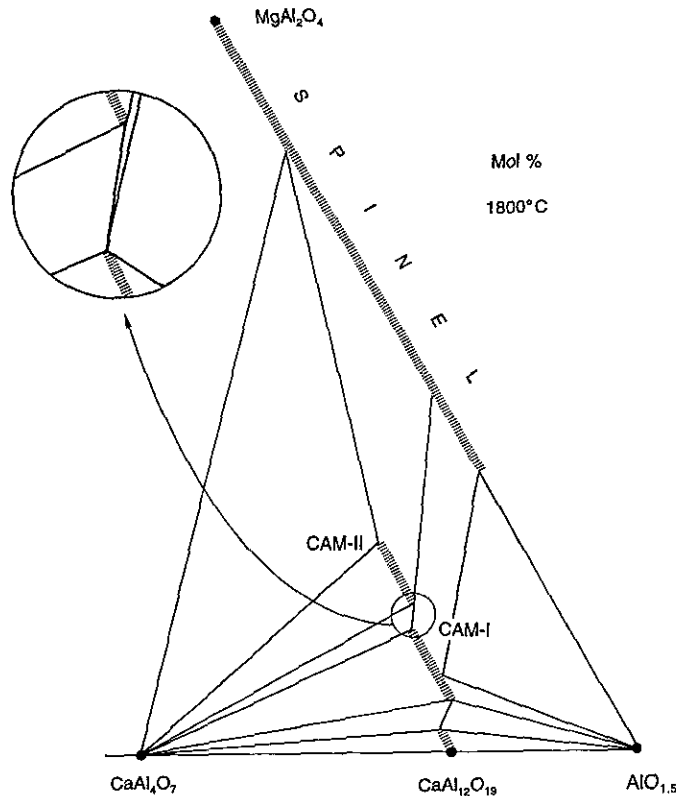
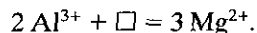


FIG. 3. Tie line relations in the Al-rich part of the system CaO–Al₂O₃–MgO at 1800°C. In high-CaO compositions an extended range of a liquid phase appears.

TABLE 3
Compositions of Liquids Coexisting with
CAM-I and CAM-II at 1800°C

Mole%	CaO	Al ₂ O ₃	MgO
CAM-I _{ss(L)}	11.1	80.0	8.9
Liquid _(CAM-I)	32.0	67.0	1.0
CAM-II _{ss(L)}	9.1	75.5	15.5
Liquid _(CAM-II)	43.5	52.9	3.6

spinel layer of the magnetoplumbite structure according to the reaction



An increase of MgO above this limit results in the formation of a new phase, CAM-I_{ss}, by the intercalation of an additional spinel layer in the structure, which itself is characterized by a high concentration of cation defects in the low-Mg end of the CAM-I_{ss} series. With increasing magnesium concentrations these defects are again filled up, following the above exchange reaction, until all lattice sites of the layer are fully occupied. Further addition of magnesia results again in the intercalation of another spinel layer in CAM-II_{ss}, following the same rules as in CAM-I_{ss}. The end of the magnetoplumbite series in the CaO–Al₂O₃–MgO system is attained as soon as all defects in the second layer are eliminated.

A structure determination of CAM-I and CAM-II will be presented in Part II of this paper.

From the fact that the phases CAM-I and CAM-II in the system CaO–Al₂O₃–MgO are structurally correlated to the phases *X* and *W* in the system BaO–Fe₂O₃–ZnO (1), it may be concluded that even more magnetoplumbite phases exist in related systems. Accordingly, other systems are presently being investigated.

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