The Aluminum-Rich Part of the System BaO–Al$_2$O$_3$–MgO

I: Phase Relationships

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The subsolidus phase relations in the Al-rich part of the system BaO–Al$_2$O$_3$–MgO at 1800°C in air have been determined. The hexaaluminate phases in this part of the system all exhibit β-alumina structure types. In the binary system BaO–Al$_2$O$_3$, the phases Ba$_{1.21}$Al$_{11}$O$_{17.71}$ and Ba$_{0.75}$Al$_{11}$O$_{17.25}$ were confirmed. In the ternary system, two solid solution series, BAM-I and BAM-II, exist. The solid solution range of BAM-I between the defect-free β-alumina end member BaMgAl$_{10}$O$_{17}$ and the Mg-free end member Ba$_{0.75}$Al$_{11}$O$_{17.25}$ can be described by the formula Ba$_{1-x/4}$Mg$_{1-x}$Al$_{10+x}$O$_{17+x/4}$ ($0 \leq x \leq 1$). The solid solution series BAM-II contains higher Mg concentrations. It can be expressed by the formula Ba$_2$Mg$_{6-3y}$Al$_{28+2y}\square_y$O$_{50}$ ($O \leq y \leq 0.3$). The Mg-rich end member of BAM-II is plotted exactly at the join between the defect-free end member of BAM-I and the stoichiometric Mg–Al–spinel. Thus it is concluded that the structure of BAM-II is a mixed-layer model containing both structure units. © 1998 Academic Press

INTRODUCTION

The group of hexaaluminates exhibits interesting compounds, e.g. for solid state electrolytes and for optical applications in the field of luminescent materials, lasers, etc … . The crystal structure present is defined by crystal chemical aspects. Subsequently physical properties can be derived. In hexaaluminates containing divalent cations two major structure types can be distinguished: β-alumina- and magnetoplumbite-based structures (1, 2). Both types are layer structures consisting of spinel blocks and so-called "conduction layers" stacked alternating along the c direction. The difference in the atomic arrangement in the conduction layer defines the structure type present.

Structure determinations of hexaaluminates containing Ca revealed the existence of the magnetoplumbite structure type phase hibonite (CaAl$_{12}$O$_{19}$) (3). In the ternary system CAO–Al$_2$O$_3$–MgO, the addition of Mg resulted in the formation of magnetoplumbite-based mixed-layer struc-

tures in the phases CAM-I (Ca$_2$Mg$_2$Al$_{28}$O$_{46}$) and CAM-II (CaMg$_2$Al$_{16}$O$_{27}$) (3, 4). In case of hexaaluminates containing Sr, the magnetoplumbite phase Sr hexaaluminate (SrAl$_{12}$O$_{19}$) is stable. In the system SrO–Al$_2$O$_3$–MgO, two discrete phases are found. With higher Mg concentrations a β-alumina phase SAM-II (SrMgAl$_{10}$O$_{17}$) forms, while with intermediate Mg concentrations a phase SAM-I (Sr$_2$MgAl$_{22}$O$_{36}$) combining both structure types with alternating β-alumina and magnetoplumbite layers is stable (5).

In the present paper, phase assemblages and possible solid solution ranges in the Al-rich part of the system BaO–Al$_2$O$_3$–MgO at 1800°C will be investigated in detail.

PREVIOUS WORK

In the Al-rich part of the system BaO–Al$_2$O$_3$, two phases have been reported. Ba$_{1.21}$Al$_{11}$O$_{17.71}$ represents a collapsed β-alumina structure, while Ba$_{0.75}$Al$_{11}$O$_{17.25}$ is a β-alumina containing defects (6–13).

In the system BaO–Al$_2$O$_3$–MgO three phases, BaMgAl$_{10}$O$_{17}$, BaMg$_2$Al$_{14}$O$_{24}$, and BaMg$_3$Al$_{14}$O$_{25}$, have been reported where BaMgAl$_{10}$O$_{17}$ is identified as a β-alumina (14, 15).

In the binary system MgO–Al$_2$O$_3$ only the Mg–Al–spinel (MgAl$_2$O$_4$) with a rather wide solid solution range at high temperatures is stable (16–18).

EXPERIMENTAL METHODS

To determine the phase relations in the ternary system BaO–Al$_2$O$_3$–MgO appropriate mixtures of selected samples were prepared by conventional methods. Starting with high-purity reagents ($>99.9\%$) of Al$_2$O$_3$, BaO, and MgO, the mixtures considering the weight loss were homogenized under acetone in agate mortars, dried, and heated to 1100°C for 12 h followed by milling in a tungsten carbide ball mill. Small samples were equilibrated at different temperatures in the range of 1500 to 1850°C for 48 to 2 h depending on the presence or absence of a melt. The equilibration

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experiments were carried out in a vertical molybdenum-wound tube furnace with a commercial Eurotherm electronic temperature controller.

For measuring the temperature up to 1600°C a $Pt/Pt_{90}Rh_{10}$ thermocouple was used, and up to 1850°C, a $Pt_{80}Rh_{20}/Pt_{60}Rh_{40}$ thermocouple was used. The calibrations were performed against the melting points of diopside ($CaMgSi_2O_6$) at 1393.5°C, pseudowollastonite ($CaSiO_3$) at 1546°C, platinum at 1772°C, and the formation of two immiscible liquids in the mixture 93 mol% SiO_2, 7 mol% CaO (19) at the invariant temperature of 1710°C. The quoted temperatures correspond to the IPTS-68 temperature scale.

The equilibration experiments were carried out in air. Quenching was performed by dropping the sample on a thick brass block with a high heat capacity. Water was not used for quenching to avoid possible reactions.
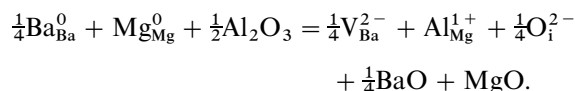
The quenched products were prepared and studied by reflected light microscopy. Selected samples were analyzed by electron probe microanalysis (EPMA) with Cameca Camebax equipment using the ZAF evaluation program. The backscattered electron image of the samples enabled the distinction of the phases and suitable grains of sufficient size could be selected. Series of measurements of coexisting phases in mutual contact were performed. Only analyses of a total within the range of $100 \pm 2\%$ were taken into consideration.

Selected samples were used to obtain powder patterns by X-ray diffractometry. A Philips PW 1820 diffractometer with $CuK\alpha$ radiation and Si as an external standard were used.

FIG. 1. EPMA data in the Al-rich part of the system BaO–Al_2O_3–MgO taken from samples equilibrated at 1800°C.

RESULTS

In the Al-rich part of the binary system BaO–Al_2O_3, no phase with magnetoplumbite structure is stable. Instead $Ba_{1.21}Al_{11}O_{17.71}$ and $Ba_{0.75}Al_{11}O_{17.25}$ with structures related to the β-alumina-type were confirmed.

In Fig. 1 selected microprobe analyses on samples in the ternary system BaO–Al_2O_3–MgO equilibrated at 1800°C are plotted. They reveal the solid solution series BAM-I and BAM-II. BAM-II$_{ss}$ extends between the Mg-free end member $Ba_{0.75}Al_{11}O_{17.25}$ and the Mg-rich end member $BaMgAl_{10}O_{17}$. The Mg-free end member exhibits a β-alumina structure with a high defect concentration. This defect concentration is reduced by the addition of Mg. The substitution mechanism following the Kröger–Vink (21) notation is

$$\tfrac{1}{4}Ba_{Ba}^0 + Mg_{Mg}^0 + \tfrac{1}{2}Al_2O_3 = \tfrac{1}{4}V_{Ba}^{2-} + Al_{Mg}^{1+} + \tfrac{1}{4}O_i^{2-}$$
$$+ \tfrac{1}{4}BaO + MgO.$$

The solid solution range necessarily ends where the defect concentration is zero at the end member $BaMgAl_{10}O_{17}$.

The same mechanism has previously been found for the Sr–β-alumina phase SAM-II ($SrMgAl_{10}O_{17}$) (5). A reduction in the Mg concentration which is replaced by Al is thus accompanied by the decrease of Ba in the conduction layer forming a vacancy. The valence balance is made by the incorporation of additional O in the conduction layer not necessarily at the exact position of the former Ba. This results in a solid solution series of BAM-I:

$$Ba_{1-x/4}Mg_{1-x}Al_{10+x}O_{17+x/4}, \quad \text{with } 0 \leq x \leq 1.$$
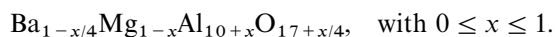
Between 1500 and 1850°C, the range of BAM-I$_{ss}$ is temperature-independent.

Another Mg-rich ternary phase, BAM-II, exhibits a limited solid solution range. Due to the high Mg content and the consequently sluggish reactions, this part of the phase diagram was only studied at 1800 to 1850°C. The Mg-rich end member of this solid solution range plots exactly on the join between the defect free BAM-I and the Mg–Al–spinel (Fig. 1). From the close structural relationship between the Ba–β-alumina phase BAM-I and spinel it is concluded that the phase BAM-II can be described by a suitable

combination of β-alumina and spinel structural units, thus forming a mixed-layer structure. Comparable mixed-layer structures have already been described in the system CaO–Al$_2$O$_3$–MgO (3, 4).

Within the solid solution range of BAM-II the Ba content is constant and the following substitution according to the Kröger–Vink notation (21) is observed:

$$3Mg^0_{Mg} + Al_2O_3 = 2Al^{1+}_{Mg} + V^{2-}_{Mg} + 3MgO.$$

This also supports the structure model for BAM-II$_{ss}$. The formula for the solid solution series can thus be expressed as

$$Ba_2Mg_{6-3y}Al_{28+2y}\square_yO_{50}, \quad with \ 0 \le y \le 0.3.$$
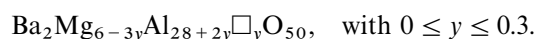
The structure determination of the phase BAM-II is presented in Part II of this report (22).

Figure 2 represents the phase relations at 1800°C. At this temperature the diagram is subsolidus throughout.

On the Ba-rich side, BAM-I$_{ss}$ coexists with Ba$_{1.21}$Al$_{11}$O$_{17.71}$, with Ba$_{1.21}$Al$_{11}$O$_{17.71}$ + Ba monoaluminate (BaAl$_2$O$_4$), or with Ba monoaluminate alone. At higher Mg contents, the three-phase field BAM-I$_{ss}$ + Ba monoaluminate + BAM-II$_{ss}$ end member with the lowest Mg content follows. BAM-II$_{ss}$ coexists with Ba monoaluminate followed by the three-phase field BAM-II$_{ss}$ + Ba monoaluminate + Mg–Al–spinel. On the Al-rich side BAM-I$_{ss}$ coexists with corundum (Al$_2$O$_3$). At higher Mg contents a three-phase field BAM-I$_{ss}$ + corundum + Mg–Al–spinel$_{ss}$, a two-phase region BAM-I$_{ss}$ + Mg–Al–spinel$_{ss}$, a three-phase field BAM-I + Mg–Al–spinel$_{ss}$ + BAM-II$_{ss}$, and finally a two-phase region BAM-II$_{ss}$ + Mg–Al–spinel$_{ss}$ exist (Table 1).

From equilibration experiments at temperatures up to 1850°C it was concluded that both BAM-I$_{ss}$ and BAM-II$_{ss}$ melt incongruently. By employing the floating zone technique for studying phase relations (20) the liquidus diagram of the Al-rich part of this system could be determined (Fig. 3). It confirmed the incongruent melting of the phases BAM-I$_{ss}$ and BAM-II$_{ss}$. Due to the fact that no exact
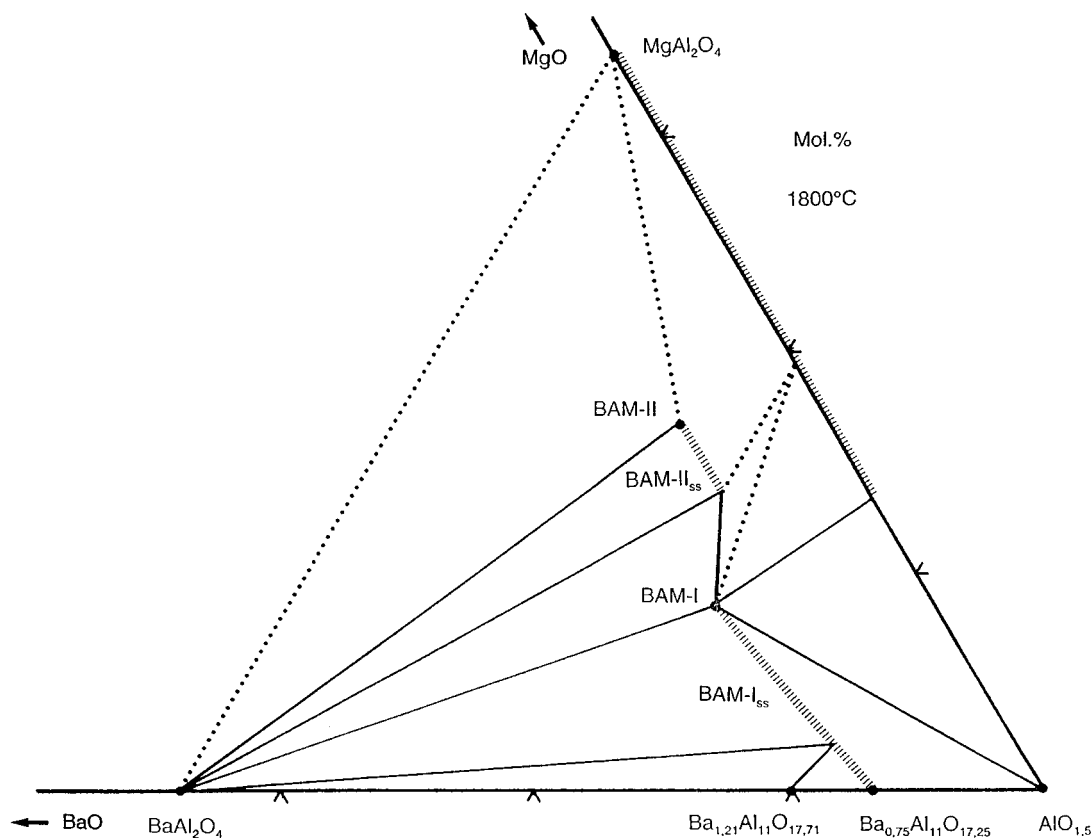

FIG. 2. Phase relations in the Al-rich part of the system BaO–Al$_2$O$_3$–MgO at 1800°C. The system is subsolidus throughout. BAM-I: Ba$_{1-x/4}$Mg$_{1-x}$Al$_{10+x}$O$_{17+x/4}$ with $0 \le x \le 1$. BAM-II: Ba$_2$Mg$_{6-3y}$Al$_{28+2y}\square_y$O$_{50}$ with $0 \le y \le 0.3$. Tie lines are given in solid and dotted lines, and solid solution series are given in hatched lines.
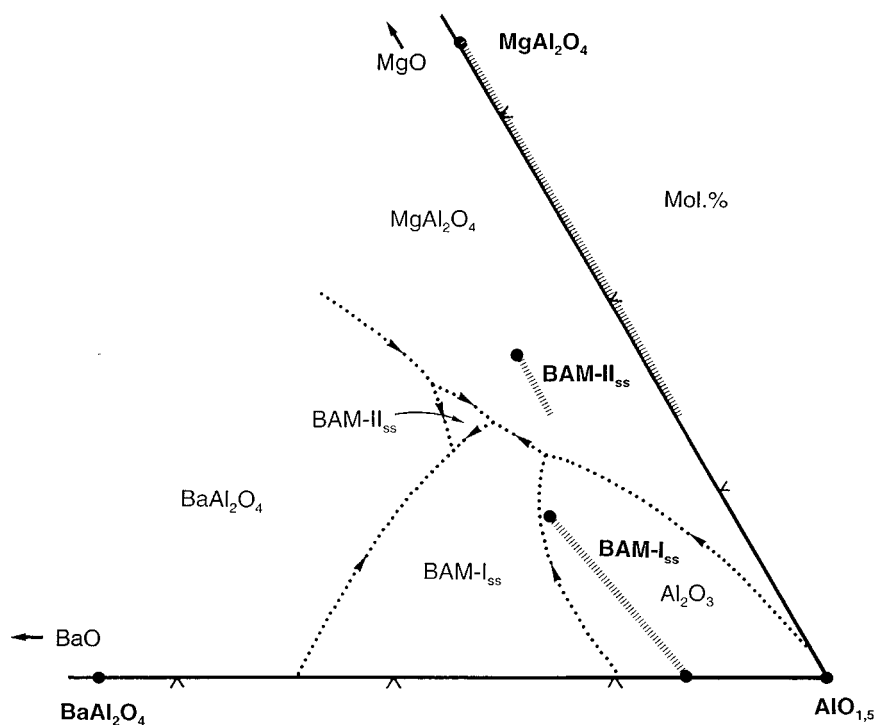
FIG. 3. Qualitative liquidus diagram of the Al-rich part of the system $BaO-Al_2O_3-MgO$.

temperature measurement during the floating zone experiment can be performed, the liquidus diagram can be given only qualitatively.

CONCLUSION

It has been shown that in the Al-rich part of the ternary system $BaO-Al_2O_3-MgO$ three solid phases are stable: $Ba_{1.21}Al_{11}O_{17.71}$, BAM-I$_{ss}$, and BAM-II$_{ss}$. The Ba aluminate phase $Ba_{1.21}Al_{11}O_{17.71}$ with a crystal structure that

has been described as a collapsed β-alumina structure was confirmed.

The $Ba_{0.75}Al_{11}O_{17.25}$ is a β-alumina with a high defect concentration. The addition of Mg results in the formation of the solid solution series BAM-I ending in the defect-free stoichiometric end member $BaMgAl_{10}O_{17}$.

The phase BAM-II$_{ss}$ ($Ba_2Mg_{6-3y}Al_{28+2y}\square_yO_{50}$) can be described as a mixed-layer structure consisting of structural units of $BaMgAl_{10}O_{17}$ and $MgAl_2O_4$. Structure determination of this phase will be presented in Part II of this paper

TABLE 1
Phase Relations and Chemical Compositions of Coexisting Phases in the Al-Rich Part of the System $BaO-Al_2O_3-MgO$ at 1800°C

Coexisting phases	BAM-I$_{ss}$ $Ba_{1-x/4}Mg_{1-x}Al_{10+x}O_{17+x/4}$	BAM-II$_{ss}$ $Ba_2Mg_{6-3y}Al_{28+2y}\square_yO_{50}$	Mg–Al–spinel $Mg_{1-3z}Al_{2+2z}\square_zO_4$
BAM-I$_{ss}$ + corundum	$0 \le x \le 1$		
BAM-I$_{ss}$ + corundum + spinel	$x = 0$		$z = 0.21$
BAM-I$_{ss}$ + spinel	$x = 0$		$0.15 \le z \le 0.21$
BAM-I$_{ss}$ + spinel + BAM-II$_{ss}$	$x = 0$	$y = 0.3$	$z = 0.15$
BAM-II$_{ss}$ + spinel		$0 \le y \le 0.3$	$0 \le z \le 0.15$
BAM-II$_{ss}$ + spinel + BaAl$_2$O$_4$		$y = 0$	$z = 0$
BaAl$_2$O$_4$ + BAM-II$_{ss}$		$0 \le y \le 0.3$	
BaAl$_2$O$_4$ + BAM-I$_{ss}$ + BAM-II$_{ss}$	$x = 0$	$y = 0.3$	
BaAl$_2$O$_4$ + BAM-I$_{ss}$	$0 \le x \le 0.8$		
BAM-I$_{ss}$ + BaAl$_2$O$_4$ + Ba$_{1.21}$Al$_{11}$O$_{17.71}$	$x = 0.8$		
Ba$_{1.21}$Al$_{11}$O$_{17.71}$ + BAM-I$_{ss}$	$0.8 \le x \le 1$		

(22). The proposed phase BaMg$_2$Al$_{14}$O$_{24}$ (14, 15) appears not to be a discrete phase but rather a member of the BAM-II solid solution series.

Ba aluminates with magnetoplumbite-type structures are not stable.

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