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Experimental and theoretical contribution to the phase equilibria in the ternary CaO-Al₂O₃-B₂O₃ system

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To the memory of Günther Effenberg

Abstract

The phase equilibria in the lime rich part of the CaO-Al₂O₃-B₂O₃ ternary system were investigated by thermodynamic modeling and key experiments. Three ternary compounds, CaAl₂B₂O₇ (CAB), Ca₂Al₂B₂O₈ (C₂AB) and Ca₂Al₂B₆O₁₄ (C₂AB₃), are reported in the literature and their thermodynamic properties were calculated using Density Functional Theory and lattice dynamics theory. Partial isothermal sections of the lime rich part of the CaO-Al₂O₃-B₂O₃ were investigated at 950°C and 1020°C using solid state reactions and X-ray diffraction on 14 selected samples. The observed results confirm the available experimental data from the literature. Based on thermal analysis using differential scanning calorimetry, the Ca₃Al₂O₆-CaB₂O₄ and CaAl₂O₄-CaB₂O₄ T-x sections as well as a tentative partial liquid surface of the lime rich part were constructed.

Key words

CaO-Al₂O₃-B₂O₃; phase equilibria; thermodynamic properties, invariant reactions; partial liquidus surface

Introduction

Small additions of boron oxide to a limestone-bauxite/kaolin-silica-calcium sulfate raw mix lead to a new class of low CO₂ hydraulic binders [1,2] now commonly cited as BYF (Belite-Ye'elimite-Ferrite) cements in the scientific literature [3]. Boron oxide plays two different roles in the clinker formulation: it stabilizes the high temperature modification of Ca₂SiO₄ (α') with higher hydraulic reactivity in the final cement and it lowers the melting point of the raw mix which makes clinkering possible at lower temperatures ($\sim 1300^\circ\text{C}$) than typically used for Ordinary Portland cement (OPC) raw mixes ($\sim 1450^\circ\text{C}$) [4]. In order to be able to control and to optimize compositions and sintering conditions for these new raw mixes, a thorough knowledge of the underlying phase equilibria is desirable. Phase diagrams of the CaO-SiO₂-Al₂O₃-Fe₂O₃-B₂O₃-SO₃ system and its sub-systems are needed. The focus in this contribution is on one of the B₂O₃ bearing sub-systems. While the phase equilibria in the lime rich part of the CaO-SiO₂-B₂O₃ ternary system are reasonably well established [5], this is not the case for the remaining ternary systems. Especially the CaO-Al₂O₃-B₂O₃ system is of interest due to the high level of alumina in BYF type clinkers. In addition, other technical applications exist for compositions in this ternary system, for example in glasses with interesting optical [6], mechanical [7] and thermal properties [8]. The potential to form glasses in the ternary CaO-Al₂O₃-B₂O₃ system is well known and the glass forming regions were investigated in the past [9]. In a recent publication by El-Hayek et al [10], the authors investigated the structure and properties of lime alumino-borate glasses in the Ca₁₂Al₁₄O₃₃ - "Ca₁₂B₁₄O₃₃" section.

Experimental information on phase equilibria in the ternary CaO-Al₂O₃-B₂O₃ system are rare. Only one experimental phase diagram study is reported in the literature (Schäfer and Kuzel [11]). They investigated the ternary equilibria by synthesizing and analyzing 60 different samples. Two new ternary compounds, CaO.Al₂O₃.B₂O₃ (CaAl₂B₂O₇) and 2CaO.Al₂O₃.B₂O₃ (Ca₂Al₂B₂O₈) were discovered. The samples were produced either by solid-state sintering or by re-crystallization of quenched amorphous liquids using CaCO₃, Al₂O₃ and H₃BO₃ as starting materials. Typical sintering/crystallization conditions were temperatures ranging from 800°C to 1000°C and isothermal heat treatments of 60 to 100h. The melting behavior of the two ternary compounds were investigated using thermal analysis. Both compounds melt incongruently at 1098 $\pm$ 10°C for Ca₂Al₂B₂O₈, forming CaAl₂O₄ + a boron oxide rich liquid and at 1015 $\pm$ 10°C for CaAl₂B₂O₇ forming Al₁₈B₄O₃₃ + a boron oxide rich liquid. The crystal structures of the ternary compounds were investigated using X-ray powder diffraction. In addition, single crystals of the ternary compounds were prepared starting from homogeneous melts followed by slow cooling of the liquid phase

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with an overall composition in the primary crystallization field of the compounds. $\text{Ca}_2\text{Al}_2\text{B}_2\text{O}_8$ has an orthorhombic unit cell with $a=8.27 \text{ \AA}$, $b=15.23 \text{ \AA}$ and $c=5.73 \text{ \AA}$. The crystal structure of this ternary compound was later refined by Schuckman to the Ccc2 space group with $a=8.269 \text{ \AA}$, $b=15.227 \text{ \AA}$ and $c=5.733 \text{ \AA}$ [12]. Ca has a 6-fold coordination, Al is in tetrahedral position and boron is surrounded by three oxygen atoms. The second ternary compound, $\text{Ca}_2\text{Al}_2\text{B}_2\text{O}_7$, exists in two different structures. The stable modification at low temperature is hexagonal with $a=4.81 \text{ \AA}$ and $c=15.55 \text{ \AA}$. The structure was later refined by Chang & Keszler [13]. For temperatures below 830°C , the crystal belongs to the R-3c space group with $a = 4.810 \text{ \AA}$ and $c= 46.633 \text{ \AA}$ in the hexagonal setting. The structure of the high temperature modification could only be determined on heat treated powder samples and the observed reflections were fitted to a monoclinic cell with $a=4.18\text{A}$, $b=15.59\text{A}$, $c= 8.16\text{A}$ and $\beta=92.3$. However, the authors were not satisfied with their fit and claimed that further experimental work on single crystals was necessary to determine the structure of the high temperature modification with the needed precision.

Based on the results on the 60 different samples, the authors constructed an isothermal section of the $\text{CaO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ diagram at 800°C (Fig.1). A third ternary compound, $\text{Ca}_2\text{Al}_2\text{B}_6\text{O}_{14}$ (also called Johachidolite) was reported in the literature. It was first discovered by Iwase & Saito [14] in natural mineral samples from North Korea. Moore & Araki [15] confirmed the existence and that it belongs to the $\text{CaO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ ternary system. They solved the crystal structure and attributed the formula $\text{Ca}_2\text{Al}_2\text{B}_6\text{O}_{14}$ to the compound. The most recent crystal structure determination was performed by Kadiyski et al [16] on natural mineral samples from Myanmar. The compound is tetragonal (Cmma) with $a=7.967(2) \text{ \AA}$, $b=11.723(2) \text{ \AA}$ and $c=4.3718(5) \text{ \AA}$. Earlier attempts to synthesize this compound artificially under atmospheric pressure conditions failed [17,18]. Kadiyski et al attributed this fact to the very dense structure and they conclude that Johachidolite may only be stable under high pressure conditions. The structural properties of the three ternary compounds are summed up in Table 1.

Table 1: Structural properties of ternary compounds in the $\text{CaO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ system

Phase / Temperature range	Space Group / Pearson symbol	Lattice parameter [Å]	Comments
$\text{Ca}_2\text{Al}_2\text{B}_2\text{O}_8$ < $1098\pm10^\circ\text{C}$	Ccc or Cccm	$a=8.27$ $b=15.23$ $c=5.73$	Schäfer & Kuzel [11] The space group is tentative

	Ccc2	a=8.269 b=15.227 c=5.733	Schluckman [12]
	Ccc2	a=8.24104 b=15.22121 c=5.74981	Calculated [this work]
LT-CaAl ₂ B ₂ O ₇ < 830°C	P6 ₃ 22	a=4.81 c=15.55	Schäfer & Kuzel [11] The space group is tentative
	R-3c	a=4.810 c=46.633	Chang & Kezler [13]
	R-3c	a=4.82093 c=46.51937	Calculated [this work]
HT-CaAl ₂ B ₂ O ₇ 830°C < T < 1015±10°C	Monoclinic	a=4.18 b=15.56 c=8.16 β=92.3	Schäfer & Kuzel [11]
Ca ₂ Al ₂ B ₆ O ₁₄	Cmma	a=7.967(2) b=11.723(2) c=4.3718(5)	Kadiyski et al [16]
	Cmma	a=7.94636 b=11.70456 c=4.36109	Calculated [this work]

Fig. 1: Experimental isothermal section of the CaO-Al₂O₃-B₂O₃ system at 800°C reproduced using the data from Schäfer and Kuzel [10]

The experimental phase diagram from Schäfer and Kuzel can be compared to a calculated isothermal section using the FactSage Gibbs energy minimizing software [19] and the FTOxid thermodynamic database in its most recent version (7.3). In the documentation of the FTOxid database, it is claimed that the Gibbs energy data for the CaO-Al₂O₃-B₂O₃ ternary system is fully assessed. The calculated isothermal section at 800°C is presented in Fig.2. The experimental and calculated diagrams differ in several points. In the calculated diagram, a lime rich liquid phase is observed in equilibrium with CaO, Ca₃Al₂O₆, CaAl₂O₄ and Ca₂B₂O₅. This liquid phase is not observed experimentally and its existence is highly unlikely because it would correspond to an extremely steep liquidus slope from pure CaO (melting point at 2949°C) to a ternary eutectic calculated at 677°C. The second difference is the absence of Ca₁₂Al₁₄O₃₃ in the calculated diagram. The third difference involves the CaAl₂B₂O₇ ternary compound. In the experimental diagram, a three phase equilibrium CaAl₂B₂O₇+CaB₂O₄+Al₄B₂O₉ is proposed while in the calculated diagram, the three phase equilibrium is CaAl₂B₂O₇+CaB₄O₇+Al₄B₂O₉. The fourth and last difference concerns the B₂O₃ rich corner for which a distinct solubility of CaO and Al₂O₃ in liquid B₂O₃ is proposed. It is obvious that the agreement between the calculated and experimental isothermal section is poor,

however it may not straightforward to judge if the difference comes from errors in the thermodynamic description or lies in the experimental determination of the diagram.

Fig.2: Calculated isothermal section of the $\text{CaO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ system at 800°C using thermodynamic data from the FTOxid database and the FactSage Gibbs energy minimizer (v.7.3) [19]. L corresponds to the liquid phase ; compounds in reduced notation $\text{C}=\text{CaO}$, $\text{A}=\text{Al}_2\text{O}_3$, $\text{B}=\text{B}_2\text{O}_3$.

The purpose of this contribution is to re-investigate experimentally the phase equilibria in the $\text{CaO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ ternary system with a focus on the lime rich part of the diagram. Phase diagram data for the three binary boundary systems were accepted from the literature. The phase diagram of the $\text{CaO-B}_2\text{O}_3$ system was established by Carlson [20]. Four solid compounds are present in the system: $\text{Ca}_3\text{B}_2\text{O}_6$, $\text{Ca}_2\text{B}_2\text{O}_5$, CaB_2O_4 and CaB_4O_7 . Data for the $\text{Al}_2\text{O}_3\text{-B}_2\text{O}_3$ binary system is less reliable. The recent review of the available experimental data and thermodynamic modeling of Decterov et al [21] was accepted for this study. Two solid compounds are present at equilibrium, $\text{Al}_{19}\text{B}_4\text{O}_{33}$ and $\text{Al}_4\text{B}_2\text{O}_9$. Additional compounds were reported in literature [22], most of them being synthesized at low temperature by sol-gel methods. It appears that these compounds transform into the two equilibrium phases when heated at higher temperatures. Two versions of the $\text{CaO-Al}_2\text{O}_3$ binary phase diagram exist in the literature. The difference is the presence or not of $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$. The compound is absent in a purified atmosphere (O_2 , N_2) [23,24], but present when

the phase diagram studies were performed in air [25,26]. The pure oxide compound $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ may therefore be the end member of the solid solution $\text{Ca}_{12}\text{Al}_{13}\text{O}_{32}(\text{O}_1(\text{OH})_2)_1$ and this end member seems to be unstable in the $\text{CaO-Al}_2\text{O}_3$ system under water free conditions.

There is no thermodynamic data available for the three ternary compounds. Therefore, their heat of formation and their heat capacities were calculated using Density Functional Theory (DFT) and lattice dynamics theory (Phonons). These theoretical data was used to calculate theoretical phase diagrams which were then compared to the experimental data.

Theory

The thermodynamic properties of the three ternary compounds, $\text{CaAl}_2\text{B}_2\text{O}_7$, $\text{Ca}_2\text{Al}_2\text{B}_2\text{O}_8$ and $\text{Ca}_2\text{Al}_2\text{B}_6\text{O}_{14}$, with respect to their constitutive simple oxides, CaO , Al_2O_3 and B_2O_3 , were determined using density functional theory (DFT) [27,28] as implemented in the VASP (Vienna Ab-Initio Software) package [29,30]. The most recent version of VASP (5.4.4) was used for this study.

The recently developed semi-local density functional SCAN (Strongly Constrained and Appropriately Normed) [31] was used here to determine the ground state properties of all compounds at 0K. The SCAN functional is known to allow more accurate total energy calculations in oxide systems as compared to results obtained with classical GGA or LDA functionals [32]. For Ca, the 3p, 3s and 4p orbitals, for Al, the 3p and 3s orbitals and for B and O, 2p and 2s orbitals are considered as valence states in the calculation. The cut-off energy for the projector augmented bands was set to 700eV. A gamma-centered k-point grid in the irreducible part of the Brillouin zone was used. This grid was automatically generated and follows the Monkhorst-Pack scheme [33]. The k-points grids for the compounds were: 10x10x1 for $\text{CaAl}_2\text{B}_2\text{O}_7$, 4x2x6 for $\text{Ca}_2\text{Al}_2\text{B}_2\text{O}_8$ and 2x2x5 for $\text{Ca}_2\text{Al}_2\text{B}_6\text{O}_{14}$. Lattice parameters and internal atomic coordinates were fully relaxed. The electronic density of state (DOS) was calculated using the linear tetrahedron method with Blöchl corrections [34]. The relaxation calculations were performed with an energy criterion of 10^{-8} eV/Å. Zero-point energies (ZPE) and derived heat capacities at constant volume (harmonic approximation) and pressure (quasi-harmonic approximation) were determined using lattice dynamics theory. Phonon spectra of all compounds were calculated using the frozen phonon / supercell method as implemented in phonopy [35]. The supercells were 1x1x2 for $\text{CaAl}_2\text{B}_2\text{O}_7$, 4x2x6 for $\text{Ca}_2\text{Al}_2\text{B}_2\text{O}_8$ and 3x2x5 for $\text{Ca}_2\text{Al}_2\text{B}_6\text{O}_{14}$. The convergence criteria for the Hellman-Feynman forces was set to 10^{-6} eV/Å to avoid any kind of residual stress in the lattice.

Experimental

The raw material for CaO was pure limestone CaCO_3 (99%, GPR Reactapur - VWR Prolabo) and for Al_2O_3 pure corundum (99%, VWR Prolabo). Concentrated boron compounds are classified as carcinogenic, mutagenic or toxic to reproduction (CMR) and therefore boric acid H_3BO_3 was avoided as starting material. Because the purpose of the study is to investigate lime-rich compositions, it was decided to use solid Calcium metaborate CaB_2O_4 (39-44% B_2O_3 , Sigma Aldrich) instead. The boron content of the sample was checked by ICP analysis and a value of 39.6% was found which is within the specification given by the supplier.

Pure $\text{Ca}_3\text{Al}_2\text{O}_6$ and CaAl_2O_4 were prepared for further processing. Appropriate amounts of CaCO_3 and Al_2O_3 were mixed under wet conditions and pressed into pellets. The pellets were then dried for 12h at 105°C and fired in a static muffle furnace in air with a two-step temperature profile. The first step was identical for the two samples and corresponds to the calcination of limestone. An isothermal treatment of 1h at 900°C led to the complete loss of $\text{CO}_2(\text{g})$. The sintering step was performed at 1450°C and 12h for $\text{Ca}_3\text{Al}_2\text{O}_6$ and at 1500°C and 12h for CaAl_2O_4 followed by slow air-cooling in the furnace. Metallic crucibles with lids made of Pt-10%Rh were used for the sintering and all heat treatments to avoid any contamination and to minimize evaporation of boron. No reaction between the samples and the crucible were observed. Weight losses were recorded as the difference in initial and final weight of all sample in all experiments to estimate any boron evaporation. The cooled samples were ground in an agate mortar to a fineness $< 63\mu\text{m}$ for further processing. The purity of the samples was checked with X-Ray diffraction using the $\text{K}\alpha$ radiation of a Cu tube in θ - 2θ mode.

For the phase diagram study as a function of temperature, sample compositions were defined along two sections, $\text{Ca}_3\text{Al}_2\text{O}_6$ - CaB_2O_4 and CaAl_2O_4 - CaB_2O_4 . Appropriate amounts of ground samples of the Ca-aluminates and the Ca-metaborate were mixed together and pressed into pellets. The composition of the sample as well as the thermal treatment conditions are summed up in Table 2.

Table 2: Compositions (C=CaO, A=Al₂O₃, B=B₂O₃) and experimental conditions for all samples used in this contribution

	wt. %			Thermal treatment	
Sample	CaO	B ₂ O ₃	Al ₂ O ₃	T [°C]	Holding time [h]
90CA_10CB	36.4	5.5	58.1	950	240
80CA_20CB	37.3	11.1	51.6	950	240
50CA_50CB	40.0	27.7	32.3	950	240
30CA_70CB	41.9	38.8	19.4	950	240
85C3A_15CB	59.6	8.3	32.1	950	240
75C3A_25CB	57.9	13.8	28.3	1020	90
68C3A_32CB	56.6	17.7	25.7	1020	90
60C3A_40CB	55.2	22.2	22.6	1020	90
50C3A_50CB	53.4	27.7	18.9	1020	90
40C3A_60CB	51.7	33.2	15.1	950	240
30C3A_70CB	49.9	38.8	11.3	950	240
Ter_70C_10B_20A	69.9	10.2	19.9	1020	90
Ter_30C_55B_55A	25.1	15.0	54.9	1020	90
Ter_25C_25B_50A	25.1	24.9	50.0	1020	90

In addition, three ternary compositions as well as the two reported stable ternary compounds, Ca₂Al₂B₂O₈ and CaAl₂B₂O₇ were prepared by weighing and mixing appropriate amounts of CaCO₃, Al₂O₃ and CaB₂O₄. The different raw mixes were pressed into pellets and sintered at 1020°C for 190h. The mineralogical compositions of all samples were determined by X-ray diffraction.

Thermal analysis was performed on all samples using a Setaram Setsys Evolution apparatus and the DSC (Differential Scanning Calorimetry) measuring tip. The equipment was calibrated on temperature with the fusion temperatures of NaCl, KCl, K₂SO₄ and CaF₂. A typical amount of 50mg of each sample was placed in platinum crucibles and covered with a platinum lid. All measurements were performed with a heating rate of 5K/min from room temperature up to 1450°C directly followed by a cooling step with the same rate and under flowing Ar with a flow rate of 20 mL/min. The baseline correction was performed by a thermal run with empty crucibles in both measurement chambers. The estimation of the experimental error of all measured temperatures in this contribution is ±5K. The reported invariant temperatures correspond to the

onset of the endothermal peaks in the heat flow curves. The liquidus temperatures correspond to the return to the baseline at high temperature. The exact values were determined by derivation of the heat flow curve.

Results and discussion

Thermodynamic properties

The calculated lattice parameters corresponding to the fully relaxed atomic positions in the three ternary compounds are presented in Table 1. The overall agreement with the experimentally observed lattice parameters is good.

The calculated ground state energies and zero-point energies (ZPE) for the simple oxides and the three ternary compounds are presented in Table 3. The energy of formation $\Delta E(0K)$ of all three ternary compounds are negative, i.e. they are stable at 0K with respect to the three constituting simple oxides in their respective ground state.

Table 3 : Thermodynamic properties at 0K from DFT calculations using the SCAN functional

Compound	E(0K) [kJ/mol]	ZPE [kJ/mol]		
CaO	-2157.258	10.010		
Al ₂ O ₃	-4929.612	45.545		
B ₂ O ₃	-4488.856	64.163		
			$\Delta E(0K)$ [kJ/mol]	$\Delta ZPE(0K)$ [kJ/mol]
CaAl ₂ B ₂ O ₇ (CAB)	-11680.181	114.935	-104.455	-4.783
Ca ₂ Al ₂ B ₂ O ₈ (C ₂ AB)	-13902.534	126.747	-168.710	-2.982
Ca ₂ Al ₂ B ₆ O ₁₄ (C ₂ AB ₃)	-23042.385	256.340	-331.688	-1.715

The heat capacity at constant pressure in the quasi-harmonic approximation, as compared to Neumann & Kopp's additive rule are presented in Figures 3-5 for the three ternary compounds.

Fig 3: Calculated heat capacity at constant pressure in the quasi-harmonic approximation for $\text{CaAl}_2\text{B}_2\text{O}_7$ (full line) as compared to Neumann-Kopp's additive rule (dotted line) using data from the Factsage pure substance database for CaO , Al_2O_3 and B_2O_3 .

Fig 4: Calculated heat capacity at constant pressure in the quasi-harmonic approximation for $\text{Ca}_2\text{Al}_2\text{B}_2\text{O}_8$ (full line) as compared to Neumann-Kopp's additive rule (dotted line) using data from the Factsage pure substance database for CaO , Al_2O_3 and B_2O_3 .

Fig 5: Calculated heat capacity at constant pressure in the quasi-harmonic approximation for $\text{Ca}_2\text{Al}_2\text{B}_6\text{O}_{14}$ (full line) as compared to Neumann-Kopp's additive rule (dotted line) using data from the Factsage pure substance database for CaO , Al_2O_3 and B_2O_3 .

For $\text{CaAl}_2\text{B}_2\text{O}_7$ and $\text{Ca}_2\text{Al}_2\text{B}_2\text{O}_8$ the calculated heat capacity is close to the sum of the simple oxides up to $\sim 350\text{K}$. At higher temperatures, the calculated heat capacity is below the Neumann & Kopp's one. As already mentioned above, there is unfortunately now experimental data available with which the calculated theoretical values could be compared. However, as the atomic positions in both structures are not high symmetry ones [12,13], anharmonic contributions are likely to occur at higher temperatures. The calculated heat capacity at temperatures above 350K may therefore act as a lower boundary to the true heat capacity at high temperature.

In the case of $\text{Ca}_2\text{Al}_2\text{B}_6\text{O}_{14}$, the situation is different. Already at room temperature, the heat capacity is $\sim 15\text{ J/mol K}$ below the additive rule curve. This difference remains almost the same value at higher temperature.

From the low temperature heat capacity in the $0\text{-}298\text{K}$ interval, one can derive the standard entropy at 298K and the heat content $H(298\text{K})-H(0\text{K})$ by numerical integration of the calculated values. The thermodynamic properties in the standard state are presented in Table 4. The thermodynamic properties referred to the simple oxides and compared to the commercial Factsage databases (FTPs/FTOxid) are gathered in Table 5. The thermodynamic data for the simple oxides were again taken from the Factsage pure substance database.

Table 4: Standard thermodynamic properties for the ternary compounds from DFT and phonon calculations. The data for the pure components CaO, Al₂O₃ and B₂O₃ were taken from the Factsage pure substance database.

compound	ΔH kJ/mol	S J/molK	Cp J/molK	H(298)-H(0) kJ/mol
CaO	-635.090	37.75	42.12	6.749
Al ₂ O ₃	-1678.700	50.82	79.02	10.020
B ₂ O ₃	-1271.900	53.95	65.59	9.293
CaAl ₂ B ₂ O ₇	-3687.834	181.83	185.85	30.156
Ca ₂ Al ₂ B ₂ O ₈	-4385.479	227.65	227.20	36.805
Ca ₂ Al ₂ B ₆ O ₁₄	-7099.743	257.56	335.46	46.637

Table 5: Thermodynamic properties of the three ternary compounds as referred to the simple oxides and compared to the values stored in the commercial Factsage databases (FTPs/FTOxid) .

compound	ΔH kJ/mol	ΔS J/molK	ΔCp J/molK	Reference
CaAl ₂ B ₂ O ₇	-105.14	39.31	2.16	This work
	-143.81	13.30	-0.69	FTPS 7.3
Ca ₂ Al ₂ B ₂ O ₈	-167.70	47.38	1.49	This work
	-218.22	13.30	-0.69	FTPS 7.3
Ca ₂ Al ₂ B ₆ O ₁₄	-338.16	-30.61	-15.522	This work

Using this new thermodynamic data for the ternary compounds, one can calculate the phase equilibria in the ternary CaO-Al₂O₃-B₂O₃ system. The calculated isothermal section at 25°C is presented in Fig.6 and the one calculated at 950°C in Fig 7. For the high temperature, the validity of Neumann-Kopp’s rule was assumed for the heat content of CaAl₂B₂O₇ and Ca₂Al₂B₂O₈ (i.e. ΔCp=0 with respect to the simple oxides) and for Ca₂Al₂B₆O₁₄ the constant ΔCp reported in Table 5 was

adopted in the full temperature range. The Gibbs energy data for the binary compounds for the phase diagram calculations were taken from the Factsage substance database.

Fig. 6 : Calculated isothermal section of the CaO-Al₂O₃-B₂O₃ system at 25°C (C=CaO, A=Al₂O₃, B=B₂O₃)

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Fig 7: Calculated isothermal section of the CaO-Al₂O₃-B₂O₃ system at 950°C (C=CaO, A=Al₂O₃, B=B₂O₃)

At low temperature, Ca₂Al₂B₆O₁₄ is the only stable ternary compound in the system. At 950°C, Ca₂Al₂B₆O₁₄ is no longer present. CaAl₂B₂O₇ and Ca₂Al₂B₂O₈ are stable and the calculated diagram is in agreement with the experimental work of Schäfer & Kuzel [11] in the lime rich part. The only difference is the CaB₂O₄-Al₄B₂O₉ equilibrium which is observed experimentally but could not be reproduced in the calculation.

The origin of this occurrence / decomposition behavior of the three ternary phases lies in their large difference in entropy. As can easily be seen from data in Table 4, CaAl₂B₂O₇ and Ca₂Al₂B₂O₈ have largely positive entropies of formation with respect to the simple oxides. These two ternary compound are entropy stabilized and their Gibbs energy becomes more negative with temperature. In the case of Ca₂Al₂B₆O₁₄, the calculated standard entropy is formation with respect to the simple oxides is negative, i.e. the Gibbs energy becomes less negative with temperature. One can calculate the decomposition/formation temperatures for the three compounds: 461°C for CaAl₂B₂O₇, 495°C for Ca₂Al₂B₂O₈ and 609°C for Ca₂Al₂B₆O₁₄. Due to the uncertainty in the heat capacity at higher temperature, these values are only indicative and must be confirmed by additional experiments.

Kadiyski et al [16] suspected Ca₂Al₂B₆O₁₄ to be a high pressure phase. This seems not to be the case as our calculations indicate that it is the stable compound at room temperature. However, the experimental verification of the phase stability may be difficult to obtain in a reasonable amount of time due to the sluggish formation kinetics at low temperature.

Experimental phase equilibria

The mineralogical composition of all samples are presented in Table 6. The observed weight loss during the thermal treatments is small (below 0.3%) indicating that boron evaporation is negligible. Based on this data, partial isothermal sections (lime rich part) of the CaO-Al₂O₃-B₂O₃ ternary system were constructed at 950°C (Fig. 8) and 1020°C (Fig.9). The equilibria presented here agree with the work from Schäfer and Kuzel [11]. Only the two known ternary compounds CaAl₂B₂O₇ and Ca₂Al₂B₂O₈ were detected in agreement with the calculated diagram in Fig. 7. The third reported ternary compound, Ca₂Al₂B₆O₁₄ is apparently not stable under our experimental conditions. It is important to mention that in both cases, Ca₁₂Al₁₄O₃₃ was detected as equilibrium phase. The thermal treatments were performed in air and the origin of the occurrence may be the moisture content in the air.

Table 6: Phase composition of samples using X-ray powder diffraction (C=CaO, B=B₂O₃, A=Al₂O₃).

Phases in brackets are present as traces only.

Sample	Identified phases
90CA_10CB	CaAl ₂ O ₄ , Ca ₃ B ₂ O ₆ , CaAl ₄ O ₇
80CA_20CB	Ca ₃ B ₂ O ₆ , CaAl ₄ O ₇ , Ca ₂ Al ₂ B ₂ O ₈
50CA_50CB	Ca ₂ Al ₂ B ₂ O ₈ , CaAl ₂ B ₂ O ₇ , Ca ₂ B ₂ O ₅
30CA_70CB	CaAl ₂ B ₂ O ₇ , Ca ₂ B ₂ O ₅ , CaB ₂ O ₄
85C3A_15CB	Ca ₃ Al ₂ O ₆ , Ca ₁₂ Al ₁₄ O ₃₃ , Ca ₃ B ₂ O ₆
75C3A_25CB	Ca ₁₂ Al ₁₄ O ₃₃ , Ca ₃ B ₂ O ₆ , (Ca ₃ Al ₂ O ₆), (CaAl ₂ O ₄)
68C3A_32CB	Ca ₁₂ Al ₁₄ O ₃₃ , Ca ₃ B ₂ O ₆ , CaAl ₂ O ₄ , (CaAl ₄ O ₇)
60C3A_40CB	Ca ₃ B ₂ O ₆ , CaAl ₄ O ₇ , Ca ₂ Al ₂ B ₂ O ₈ , (Ca ₁₂ Al ₁₄ O ₃₃)
50C3A_50CB	Ca ₃ B ₂ O ₆ , Ca ₂ Al ₂ B ₂ O ₈ , Ca ₂ B ₂ O ₅ , (CaAl ₄ O ₇), (Ca ₁₂ Al ₁₄ O ₃₃)
40C3A_60CB	Ca ₂ Al ₂ B ₂ O ₈ , Ca ₂ B ₂ O ₅ , CaAl ₂ B ₂ O ₇
30C3A_70CB	Ca ₂ B ₂ O ₅ , CaAl ₂ B ₂ O ₇ , CaB ₂ O ₄
Ter_70C_10B_20A	Ca ₃ Al ₂ O ₆ , Ca ₃ B ₂ O ₆ , CaO
Ter_30C_55B_55A	CaAl ₄ O ₇ , Ca ₂ Al ₂ B ₂ O ₈ , CaAl ₁₂ O ₁₉
Ter_25C_25B_50A	Ca ₂ Al ₂ B ₂ O ₈ , CaAl ₂ B ₂ O ₇ , Al ₂ O ₃

Fig.8: Partial isothermal section of the CaO-rich corner of the $\text{CaO}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3$ system at 950°C with experimental points (C=CaO, A= Al_2O_3 , B= B_2O_3)

Fig.9: Partial isothermal section of the CaO-rich corner of the CaO-Al₂O₃-B₂O₃ system at 1020°C with experimental points (C=CaO, A=Al₂O₃, B=B₂O₃)

The heat effects recorded during the DSC measurements could only be evaluated on the first heating cycle. Considerable undercooling is observed especially in the boron rich samples. Therefore, only the measured temperatures of the first heating step are reported here. The observed temperatures of the invariant reactions and the liquidus are summed up in Table 7 together with the observed weight loss in the DSC measurements. Based on these observed temperatures, tentative T-x sections were drawn including the experimental data points of the heat effects (Fig. 10 & 11). Only the solid-solid equilibria and the measured invariants were drawn. It would have been speculative to add liquidus lines with the few available experimental data points in the boron rich part of the diagrams. The weight loss after the DSC experiment (complete fusion of the sample at high temperature) in all samples is small (less than 1.2%) which indicates that the boron evaporation for the complete measuring cycle is also small. Based on the measurements, the corresponding invariant reactions were tentatively derived and are summed

up in Table 8. If different measured temperatures exist for the same invariant, a mean temperature was calculated from the individual data points. A tentative liquids surface was also constructed and is presented Fig. 12. It is important to mention, that the liquidus surface is only schematic with arbitrary units for composition. It is not possible to derive the exact compositions for liquid phase from our measurements alone. Further work is needed to determine the exact shape and compositions for the liquidus relations.

Table 7: Recorded temperatures of the measured heat effects and observed weight loss during DSC experiments

sample	In/mono variant 1 [°C]	In/mono variant 2 [°C]	In/mono variant 3 [°C]	Liquidus [°C]	Observed weight loss [%]
90CA_10CB	1241				0.9
80CA_20CB	1074	1237			1.0
50CA_50CB	986			1095	1.1
30CA_70CB	950			1068	1.2
85C3A_15CB	1257	1287			0.9
75C3A_25CB	1255	1278	1310	1322	0.9
60C3A_40CB	1078	1226		1253	1.2
50C3A_50CB	1085			1165	1.2
40C3A_60CB	984	1051		1181	1.1
30C3A_70CB	950			1370	0.8
Ter_70C_10B_20A	1285	133			1.1
Ter_30C_15B_55A	1090				0.2
Ter_25C_25B_50A	1017	1073			1.0
C ₂ AB (CaAlBO ₄)	1093				1.1
CAB (CaAl ₂ B ₂ O ₇)	1053			1240	0.6

Fig. 10: $\text{Ca}_3\text{Al}_2\text{O}_6$ - CaB_2O_4 T-x section with experimental points (x=weight fraction, C=CaO, A= Al_2O_3 , B= B_2O_3)

Fig. 11: CaAl_2O_4 - CaB_2O_4 T-x section with experimental points (x=weight fraction ; C=CaO, A= Al_2O_3 , B= B_2O_3)

Fig.12: Tentative liquids surface (arbitrary units) of the CaO-rich corner of the CaO-Al₂O₃-B₂O₃ system based on the results of the phase analyses and the DSC measurements.

Table 8: Tentative invariant reactions in the CaO-rich corner of the CaO-Al₂O₃-B₂O₃ system based on the results of the DSC measurements. The experimental uncertainties are estimated to $\pm 5\text{K}$

Reaction	Type	Temperature [°C]
$\text{Ca}_3\text{Al}_2\text{O}_6 + \text{Ca}_3\text{B}_2\text{O}_6 = \text{CaO} + \text{Liq}$	U ₁	1330
$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33} + \text{Ca}_3\text{B}_2\text{O}_6 = \text{Ca}_3\text{Al}_2\text{O}_6 + \text{Liq}$	U ₂	1257
$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33} + \text{Ca}_3\text{B}_2\text{O}_6 + \text{CaAl}_2\text{O}_4 = \text{Liq}$	E ₁	1255
$\text{CaAl}_4\text{O}_7 + \text{Ca}_3\text{B}_2\text{O}_5 = \text{CaAl}_2\text{O}_4 + \text{Liq}$	U ₃	1241
$\text{CaAl}_4\text{O}_7 + \text{Ca}_2\text{B}_2\text{O}_5 = \text{Ca}_3\text{B}_2\text{O}_6 + \text{Liq}$	U ₄	1076
$\text{CaAl}_4\text{O}_7 + \text{Ca}_2\text{B}_2\text{O}_5 = \text{Ca}_2\text{Al}_2\text{B}_2\text{O}_8 + \text{Liq}$	U ₅	1051
$\text{CaAl}_4\text{O}_7 + \text{CaAl}_{12}\text{O}_{19} + \text{Liq} = \text{Ca}_2\text{Al}_2\text{B}_2\text{O}_8$	P ₁	1090

$\text{Ca}_2\text{B}_2\text{O}_5 + \text{CaAl}_2\text{B}_2\text{O}_7 = \text{Ca}_2\text{Al}_2\text{B}_2\text{O}_8 + \text{Liq}$	U_6	985
$\text{CaAl}_2\text{B}_2\text{O}_7 + \text{CaB}_2\text{O}_4 = \text{Ca}_2\text{B}_2\text{O}_5 + \text{Liq}$	U_7	950
$\text{CaAl}_2\text{B}_2\text{O}_7 + \text{Ca}_2\text{Al}_2\text{B}_2\text{O}_8 = \text{CaAl}_{12}\text{O}_{19} + \text{Liq}$	U_8	1073
$\text{CaAl}_2\text{B}_2\text{O}_7 + \text{Ca}_2\text{Al}_2\text{B}_2\text{O}_8 = \text{Al}_2\text{O}_3 + \text{Liq}$	U_9	1017

The starting point of this paper was to resolve the origin of the differences between the calculated and the experimentally observed diagram by Schäfer and Kuzel [11] and specially to determine the temperatures of the invariant reactions in the lime rich part of the $\text{CaO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ ternary system. From our measurements, it can now be clearly stated that the thermodynamic modeling and the underlying Gibbs energy data in the FactSage FTOxid database must be wrong. The lime-richest invariant involving CaO , $\text{Ca}_3\text{Al}_2\text{O}_6$ and $\text{Ca}_3\text{B}_2\text{O}_6$ is a U-type reaction and the observed temperature of 1330°C is more than 600K higher than the calculated value. The non-congruent melting of the two ternary compounds was confirmed. $\text{Ca}_2\text{Al}_2\text{B}_2\text{O}_8$ decomposes peritectically (P_1) to a boron richer liquid, CaAl_4O_7 and a small amount of $\text{CaAl}_{12}\text{O}_{19}$ at $1090\pm5^\circ\text{C}$ which is in good agreement with the value from Schäfer and Kuzel ($1098\pm10^\circ\text{C}$). The melting temperature for $\text{CaAl}_2\text{B}_2\text{O}_7$ of 1053°C is $\sim 40\text{K}$ higher ($1015\pm10^\circ\text{C}$). The reported temperature from Schäfer and Kuzel is most likely the invariant reaction U_9 of the two ternary compounds with Al_2O_3 at 1017°C (first heat effect of sample Ter_25C_50A_25B).

Conclusion

Partial phase equilibria in the $\text{CaO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ were investigated theoretically using thermodynamic modeling and experimentally with X-ray diffraction and Differential Scanning Calorimetry. The thermodynamic properties of the three ternary compounds were calculated using DFT and lattice dynamics theory. $\text{Ca}_2\text{Al}_2\text{B}_6\text{O}_{14}$ is the only stable ternary compound at low temperature. The two others, $\text{CaAl}_2\text{B}_2\text{O}_7$ and $\text{Ca}_2\text{Al}_2\text{B}_2\text{O}_8$ form at higher temperature through solid-solid reactions. The calculated entropy of formation of the latter two compounds with respect to CaO , Al_2O_3 and B_2O_3 is largely positive which explains this behavior. Both compounds are entropy stabilized and the Gibbs energy of formation becomes more negative with increasing temperature.

Partial experimental isothermal sections were determined at 950°C and 1020°C . The measured data agrees with earlier experimental work in the literature. The lime-rich invariant reaction involving CaO , $\text{Ca}_3\text{Al}_2\text{O}_6$ and $\text{Ca}_3\text{B}_2\text{O}_6$ is of U-type with a transformation temperature of 1330°C

instead of the calculated one of 677°C. Two T-x sections, $\text{Ca}_3\text{Al}_2\text{O}_6$ - CaB_2O_4 and CaAl_2O_4 - CaB_2O_4 were constructed and the corresponding invariant reactions identified. Thermal analysis data could only be used from the first heating step because considerable undercooling was observed during cooling for B_2O_3 samples. This was expected due to the glass forming ability of CaO - Al_2O_3 - B_2O_3 ternary compositions especially for boron rich compositions. Based on the new experimental results, a tentative partial liquidus surface of the lime rich part of the ternary diagram was constructed and corresponding invariant reactions were proposed. Further experimental work is needed to determine the exact composition of the liquid phase and to confirm the type of the invariant reactions.

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Experimental isothermal section of the CaO-Al₂O₃-B₂O₃ system at 800°C reproduced using the data from Schäfer and Kuzel [10]

235x185mm (150 x 150 DPI)

Calculated isothermal section of the CaO-Al₂O₃-B₂O₃ system at 800°C using thermodynamic data from the FTOxid database and the FactSage Gibbs energy minimizer (v.7.3) [19]. L corresponds to the liquid phase ; compounds in reduced notation C=CaO, A=Al₂O₃, B=B₂O₃.

241x190mm (150 x 150 DPI)

Calculated heat capacity at constant pressure in the quasi-harmonic approximation for $\text{CaAl}_2\text{B}_2\text{O}_7$ (full line) as compared to Neumann-Kopp's additive rule (dotted line) using data from the Factsage pure substance database for CaO , Al_2O_3 and B_2O_3 .

257x168mm (150 x 150 DPI)

Calculated heat capacity at constant pressure in the quasi-harmonic approximation for $\text{Ca}_2\text{Al}_2\text{B}_2\text{O}_8$ (full line) as compared to Neumann-Kopp's additive rule (dotted line) using data from the Factsage pure substance database for CaO, Al_2O_3 and B_2O_3 .

257x167mm (150 x 150 DPI)

Calculated heat capacity at constant pressure in the quasi-harmonic approximation for $\text{Ca}_2\text{Al}_2\text{B}_6\text{O}_{14}$ (full line) as compared to Neumann-Kopp's additive rule (dotted line) using data from the Factsage pure substance database for CaO , Al_2O_3 and B_2O_3 .

257x167mm (150 x 150 DPI)

Calculated isothermal section of the CaO-Al₂O₃-B₂O₃ system at 25°C (C=CaO, A=Al₂O₃, B=B₂O₃)

241x190mm (150 x 150 DPI)

Calculated isothermal section of the CaO-Al2O3-B2O3 system at 950°C (C=CaO, A=Al2O3, B=B2O3)

241x190mm (150 x 150 DPI)

Partial isothermal section of the CaO-rich corner of the CaO-Al₂O₃-B₂O₃ system at 950°C with experimental points (C=CaO, A=Al₂O₃, B=B₂O₃)

241x190mm (150 x 150 DPI)

Partial isothermal section of the CaO-rich corner of the CaO-Al2O3-B2O3 system at 1020°C with experimental points (C=CaO, A=Al2O3, B=B2O3)

241x190mm (150 x 150 DPI)

Ca₃Al₂O₆-CaB₂O₄ T-x section with experimental points (x=weight fraction, C=CaO, A=Al₂O₃, B=B₂O₃)

241x190mm (150 x 150 DPI)

CaAl₂O₄-CaB₂O₄ T-x section with experimental points (x=weight fraction ; C=CaO, A=Al₂O₃, B=B₂O₃)

241x190mm (150 x 150 DPI)

Tentative liquids surface (arbitrary units) of the CaO-rich corner of the CaO-Al₂O₃-B₂O₃ system based on the results of the phase analyses and the DSC measurements.

241x190mm (150 x 150 DPI)