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# Subsolidus phase relations in $CaO–In_2O_3–B_2O_3$ system and crystal structure of $CaInBO_4$

H.K. Li[a,b], G.M. Cai[a,b,*], J.J. Fan[a,b], Z.P. Jin[a,b]

[a] Science Center for Phase Diagram & Materials Design and Manufacture, Central South University, Changsha, Hunan 410083, PR China
[b] School of Materials Science and Engineering, Central South University, Changsha, Hunan 410083, PR China

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ABSTRACT

Subsolidus phase relations of $CaO–In_2O_3–B_2O_3$ system have been investigated mainly by the conventional solid-state reaction technique and powder X-ray diffraction method. There are nine definite three-phase regions under present experimental conditions. Six binary compounds and one ternary compound were found to exist in this system. Crystal structure of the ternary compound $CaInBO_4$ was determined from X-ray powder diffraction data using Rietveld method. It crystallizes in the orthorhombic space group Pnma (No. 62) with $a = 10.3120(3)$ Å, $b = 3.42519(8)$ Å, $c = 9.5150(3)$ Å, $V = 336.07(2)$ Å$^3$ and $Z = 4$. Mixed occupancies were confirmed in this structure, Ca and In atoms are distributed between two atom sites: 93.6%Ca and 6.4%In occupy one site, 93.6%In and 6.4%Ca occupy another. Two $In(Ca)O_6$ octahedra and two $Ca(In)O_7$ polyhedra are linked each other by sharing edges to form ribbons in the $a$–$c$ plane and extend infinitely along the direction of the $b$ axis. The infrared spectrum of $CaInBO_4$ has been measured, which is consistent with the crystallographic study. In general, compounds $MRBO_4$ (M and R are divalent and trivalent cations, respectively) are in a large family of monoborates with different structure types strictly depending on the relative size of the M and R ions.



## 1. Introduction

Over a long period of time, borates have been established as useful functional materials with rich crystal structure [1–3], wide transparency spectra range, and large band gap. The trivalent-metal or rare-earth-metal borates have been given intense attention because of their outstanding optical properties, for instance, $K_2Al_2B_2O_7$ (KAB) [4] for second harmonic generation or $YBO_3$, $Li_6GdB_3O_9$ and $Ba_3InB_9O_{18}$ for host of phosphor [5–7]. Our group have made systematic surveys on the $MO–R_2O_3–B_2O_3$ (M = alkaline-earth metal, R = Sc, In, rare-earth metal) systems to search for new functional materials. Very recently, we investigated subsolidus phase relations in $CaO–In_2O_3–B_2O_3$ system based on exploratory syntheses via solid-state reactions, which led to the discovery of the ternary compound $CaInBO_4$. Blasse [8] and Capponi et al. [9] have ever reported the lattice parameters of $CaInBO_4$. However, the crystal structure of $CaInBO_4$ was not reported until now. In this work, the crystal structure of $CaInBO_4$ was investigated and determined by Rietveld method, with structure $CaYBO_4$ as a reference [10]. In addition, structure types of compounds $MRBO_4$ (M = divalent cations; R = trivalent cations) were reviewed in this paper.

## 2. Experiment

Samples were synthesized by high temperature solid state reactions. Stoichiometric mixtures of $CaCO_3$ (spectral reagent), $In_2O_3$ (analytical reagent), and $H_3BO_3$ (analytical reagent) were ground into powders of 200–300 mesh in the agate mortar. The mixtures were preheated in corundum crucibles for 12 h at 600 °C to decompose $H_3BO_3$ and $CaCO_3$. Then they were cooled, reground and sintered at 800–1350 °C (depending on their compositions) for 24 h. Finally, all the samples were naturally cooled to room temperature. In all cases, special care was taken to add extra 0.2 mol% $H_3BO_3$ in order to offset the losses of $B_2O_3$ in the procedure of synthesis.

X-ray powder diffraction (powder XRD) technology, Inorganic Crystal Structure Database (ICSD release 2011) and Powder Diffraction File (PDF release 2009) were used for phase analysis of the samples. The powder XRD patterns were collected on an X-ray Rigaku diffractometer D/MAX-2500 with Cu Kα radiation and graphite monochromator operated at 40 kV, 150 mA. The samples were considered to reach phase equilibrium when their powder XRD patterns showed no change upon successive heat treatments. Data for crystal structure analysis were collected at room temperature in the step-scanning mode with a step size 0.02° (2$\theta$), counting time 2 s per step and 2$\theta$ range of 10–130°.

With the samples dissolved in nitric acid at boiling point for 1 h, the atomic ratios of Ca, In, and B for phases were measured by inductively coupled plasma atomic emission spectrometry on a Perkin Elmer ICP/6500 spectrometer.

Infrared (IR) spectroscopy was carried out with the objective of specifying and comparing the coordination of boron in the title compound. The mid-infrared

* Corresponding author at: School of Materials Science and Engineering, Central South University, Changsha, Hunan 410083, PR China. Tel.: +86 0731 88877 732.
*E-mail addresses:* gmcai2002@163.com, caigemei@csu.edu.cn (G.M. Cai).

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**Table 1**
List of phase identification in the system $CaO–In_2O_3–B_2O_3$.

| Samples | CaO (at.%) | $InO_{1.5}$ (at.%) | $BO_{1.5}$ (at.%) | Synthesis temperature | Phase composition |
|---|---|---|---|---|---|
| 1 | 20 | 5 | 75 | 800 | $CaB_6O_{10} + CaB_2O_4 + InBO_3$ |
| 2 | 40 | 5 | 55 | 950 | $Ca_2B_2O_5 + CaB_2O_4 + InBO_3$ |
| 3 | 33.3 | 22.2 | 44.5 | 1000 | $T + Ca_2B_2O_5 + InBO_3$ |
| 4 | 50 | 5 | 45 | 950 | $T + Ca_2B_2O_5 + Ca_3B_2O_6$ |
| 5 | 25 | 40 | 35 | 1200 | $T + InBO_3 + In_2O_3$ |
| 6 | 30 | 45 | 25 | 1200 | $Ca_3B_2O_6 + In_2O_3$ |
| 7 | 40 | 40 | 20 | 1200 | $Ca_3B_2O_6 + In_2O_3 + CaIn_2O_4$ |
| 8 | 60 | 25 | 15 | 1000 | $Ca_3B_2O_6 + CaO + CaIn_2O_4$ |
| 9 | 70 | 15 | 15 | 1200 | $Ca_3B_2O_6 + CaO + CaIn_2O_4$ |
| H | 33.4 | 66.6 | 0 | 1350 | $CaIn_2O_4$ |
| T | 33.3 | 33.3 | 33.4 | 1050 | $T + In_2O_3$ |

spectrum was obtained at room temperature via a Perkin-Elmer 983G infrared spectrophotometer with KBr pellets as standards. It was collected in a range from 400 to 2000 $cm^{-1}$ with a resolution of 1 $cm^{-1}$.

## 3. Results and discussion

### 3.1. Subsolidus phase relations in $CaO–In_2O_3–B_2O_3$ system

In the binary system $CaO–B_2O_3$, six binary compounds $CaB_6O_{10}$ [11], $CaB_4O_7$ [12], $CaB_2O_4$ [ICDD-PDF 76-0747], $Ca_2B_2O_5$ [ICDD-PDF 79-1516], $Ca_3B_2O_6$ [13], and $Ca_2B_6O_{11}$ [14], have been reported. In the work of Hart and Brown [15], $Ca_2B_6O_{11}$ was synthesized under a hydrothermal condition. We did not observe $CaB_4O_7$. Yet, there is a possibility that $CaB_4O_7$ decomposes into $CaB_6O_{10}$ and $CaB_2O_4$ above 800 °C. A detailed study of thermal stability of $CaB_4O_7$ will be necessary. The other four compounds were confirmed in our experiment.

In the system $CaO–In_2O_3$, two binary compounds have been reported, namely, $CaIn_2O_4$ [16], and $Ca_3In_2O_6$ [ICDD-PDF 73-0154]. According to the literature [17], Schenck and Müller-Buschbaum synthesized $Ca_3In_2O_6$ at above 2000 °C. So, only $CaIn_2O_4$ was obtained under our present work.

As for the binary system $In_2O_3–B_2O_3$, one binary compound $InBO_3$ was reported by [PDF 82-1188] and confirmed in our experiment.

Based on the phase identifications of eleven samples with different compositions as listed in Table 1, the subsolidus phase relations of $CaO–In_2O_3–B_2O_3$ system were determined under present experimental conditions, as shown in Fig. 1. There are 9 definite three-phase regions. No solid solution regions were observed in all binary and ternary compounds, and two-phase regions are all jointlines of relevant two compounds. Ternary compound, $CaInBO_4$ was found and confirmed in this system. Comparing with our work, the powder XRD pattern [9] reported in ICDD-PDF 27-1055 was found incomplete. Moreover, the crystal structure of this compound has no report in previous literatures. Thus, we reinvestigated the crystal structure of compound $CaInBO_4$, which will be discussed in the following section.

### 3.2. Crystal structure of $CaInBO_4$

Using the program DICVOL04 [18] by successive dichotomy method with Si as the internal standard, all the reflections ($2\theta \leq 50°$) of the compound $CaInBO_4$ can be well indexed on the basis of an orthorhombic unit cell with lattice parameters $a = 10.3134(9)$ Å, $b = 9.5159(7)$, and $c = 3.4243(1)$ Å. Reflection conditions with $0\,k\,l$: $k + l = 2n$, $h\,k\,0$: $h = 2n$, $h\,0\,0$: $h = 2n$, $0\,k\,0$: $k = 2n$, and $0\,0\,l$: $l = 2n$ are consistent with space group $Pn2_1a$ and Pnma. Comparisons between $CaInBO_4$ and $CaYBO_4$ in crystal system, lattice parameters and powder XRD pattern show that the two compounds may be isostructural. So we choose the space group Pnma.

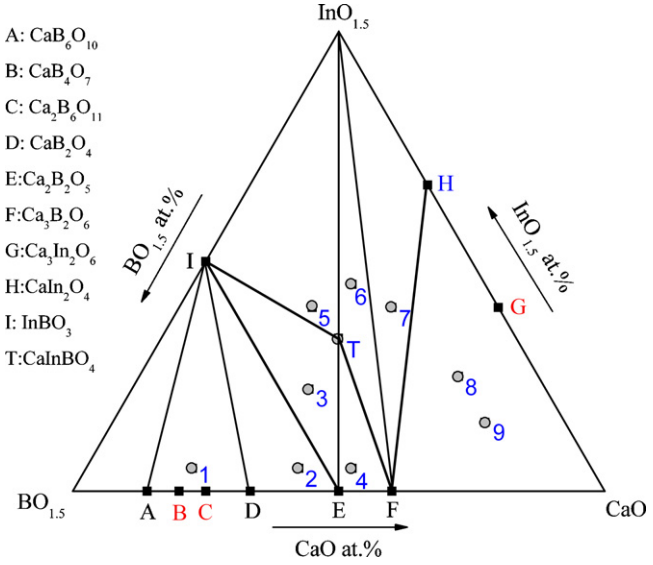


**Fig. 1.** Subsolidus phase relations in the system $CaO–In_2O_3–B_2O_3$.

In addition, there is no efficiency of second harmonic generation (SHG) in powder samples of $CaInBO_4$ using the Kurtz–Perry technique [19], which suggests centrosymmetric Pnma space group is more probable.

Taking $CaYBO_4$ as the preliminary crystal structural model, we refined the structure parameters of $CaInBO_4$ from the powder XRD data by the Rietveld method [20] using the program FullProf_suite [21]. The profile range of data used for structure refinement is 10–130° in $2\theta$, and the Pseudo-Voigt function was used as peak shape function. A total of 42 parameters were refined in the refinement, including background parameters, profile parameters, and structural parameters. As for atomic coordinates, all atoms are located on the crystal lattice position 4*c* similar to the case for $CaYBO_4$ [10]. The agreement factors in the structural refinement finally were converged to $R_B = 4.56\%$, $R_P = 7.37\%$, $R_{WP} = 10.9\%$ and $S = 2.67$, which indicates the structure model is quite right. Fig. 2 shows the final refinement pattern. Details of Rietveld refinement and crystal data are given in Table 2. Positional parameters obtained by the Rietveld refinement are listed in Table 3. By the way, we have

**Table 2**
Details of Rietveld refinement and crystal data for the structure $CaInBO_4$.

| Sample | Multi-crystal powder |
|---|---|
| Diffractometer | Rigaku D/MAX-2500 |
| Radiation type | Cu Kα |
| Monochromator | Graphite |
| Wavelength (Å) | 1.5405 |
| Refined profile range (°2θ) | 10–130 |
| Step size (°2θ) | 0.02 |
| Step scan time per step (s) | 2 |
| Number of structure parameters | 29 |
| Number of profile parameters | 13 |
| $R_B$ | 4.56% |
| $R_P$ | 7.37% |
| $R_{WP}$ | 10.9% |
| $S$ | 2.67 |
| Formula | $CaInBO_4$ |
| Symmetry | Orthorhombic |
| Space group | Pnma |
| $a$ (Å) | 10.3120(3) |
| $b$ (Å) | 3.42519(8) |
| $c$ (Å) | 9.3950(3) |
| Volume (Å$^3$) | 336.07(2) |
| $Z$ | 4 |
| Calculated density (g $cm^{-3}$) | 2.73 |