

COMBINED DTA AND XRD STUDY OF SINTERING STEPS TOWARDS $\text{YAl}_3(\text{BO}_3)_4$

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Abstract

Sintering processes in the $\text{Y}_2\text{O}_3\text{--Al}_2\text{O}_3\text{--B}_2\text{O}_3$ system and its subsystems ($\text{Y}_2\text{O}_3\text{--B}_2\text{O}_3$ and $\text{Al}_2\text{O}_3\text{--B}_2\text{O}_3$) have been investigated by using combined DTA and XRD measurements to get a better understanding of solid state chemical changes resulting in the formation of yttrium aluminum borate ($\text{YAl}_3(\text{BO}_3)_4$, YAB) phase and to study the possible role and contribution of various simple borates formed also in the former processes.

Two new exothermic heat effects of YBO_3 formation have been detected by DTA in the $\text{Y}_2\text{O}_3\text{--B}_2\text{O}_3$ system between 720 and 980°C. In the $\text{Al}_2\text{O}_3\text{--B}_2\text{O}_3$ system a new experimental XRD profile of $\text{Al}_4\text{B}_2\text{O}_9$ was observed. Formation of these borates seems to promote the nucleation of double borate YAB below 1000°C. Conversion of $\text{Al}_4\text{B}_2\text{O}_9$ to $\text{Al}_{18}\text{B}_4\text{O}_{33}$ was observed after a long term (10 h) sintering at 1050°C. Similarly, an increased formation of YAB has been observed as a product of the sintering reaction between YBO_3 and $\text{Al}_{18}\text{B}_4\text{O}_{33}$ at 1150°C. The two latter single borates are found to be identical with the high temperature decomposition products of YAB.

Keywords: DTA, sintering, thermal decomposition, XRD, yttrium aluminum borate

Introduction

Yttrium aluminum borate ($\text{YAl}_3(\text{BO}_3)_4$, YAB) crystals of high non-linear optical coefficient, especially when they are doped with neodymium [1–3], neodymium and lutetium [4, 5], or ytterbium [6, 7], are applied in diode-laser pumped self-frequency-doubling lasers in order to generate coherent visual light-beams. YAB has carbonate huntite type structure (space group R32) [8, 9] and regularly is grown from its constituent oxides in $\text{K}_2\text{Mo}_3\text{O}_{10}$ flux [10–12]. The growth process is rather sensitive, and many details of the production of optical quality single crystals have not been clarified yet. Recently, we have attempted YAB phase preparation by solid state sintering, which produced also additional single borates (YBO_3 , $\text{Al}_4\text{B}_2\text{O}_9$ and $\text{Al}_{18}\text{B}_4\text{O}_{33}$) as by-product phases at various temperatures [13]. Now we have carried

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out a more detailed investigation of chemical processes and products in the system $Y_2O_3:Al_2O_3:B_2O_3=1:3:4$ and its subsystems using combined DTA and XRD analysis. The main focus has been on the following questions. How do the formation and the reaction of the single borate compounds effect the sintered formation of the double borate phase, YAB? Are the single borates by-products only or do they behave as intermediates at higher temperature?

Experimental

The purity of the starting oxides was 99.9% for B_2O_3 and 99.99% for Y_2O_3 and $\alpha-Al_2O_3$. The oxide powders were mixed in the required ratios in aqueous acetone. After drying, these mixtures were used as powder in the DTA experiments or as pressed pellets (at 15 MPa) in the sintering experiments. The pellets were sintered in static air at atmospheric pressure in Pt crucibles at 1150°C for 10 h, and 1300°C for 2 h. Sintered pellets of YBO_3 and $Al_4B_2O_9$ were prepared at 1020°C for 30 h, while that of $Al_{18}B_4O_{33}$ at 1150°C for 10 h. Then they were powdered and used as reagents in further sintering or DTA experiments.

DTA measurements were carried out in a DuPont 990 Thermal Analyzer equipped with 1200°C DTA furnace. Pure Al_2O_3 was used as reference material. Heating rate of 10°C min⁻¹ was applied up to 1000–1100°C. Initial sample sizes were between 30–60 mg.

X-ray powder diffraction (XRD) was used for phase analysis of the samples sintered or obtained in the DTA furnace. The XRD measurements were carried out with a FPM HZG-4 type diffractometer using CuK_{α} radiation and Ni filter. The amorphous B_2O_3 has been identified after the specimen was wetted and dried, meanwhile the B_2O_3 content changed into well-crystalline H_3BO_3 (JCPDS cards No. 30-199 and 30-620).

Results and discussion

Thermal behavior and formation of YBO₃

Yttrium borate YBO_3 has a vaterite-type structure with eightfold coordination around yttrium [14–16] while the boron has probable fourfold coordination. At room temperature the crystal has a well-established X-ray diffraction pattern (JCPDS 16-277 [14]). According to the differential thermal analysis (DTA) and high temperature XRD data, YBO_3 has an unquenchable polymorphous form, too. The transition temperatures between the two forms are different on heating and cooling. These temperatures were found by DTA 1024 and 600°C, respectively [17]. It was also found, that YBO_3 shows an endothermic peak at 1020°C on heating and an exothermic peak at 580°C on cooling, when treated in repeated thermal cycles [18]. Our similar experimental curves are shown in Fig. 1.

Yttrium borate forms easily in a solid-state reaction of Y_2O_3 and B_2O_3 or H_3BO_3 . The reaction is reported to be exothermic between 600 and 700°C [18]. We have also

observed a sharp exothermic effect at 700°C. In addition, two broad and overlapping exothermic peaks not reported earlier have also occurred between 720 and 980°C (Fig. 2, curve a). These broad exothermic effects may be related to the complete conversion of B_2O_3 and Y_2O_3 into YBO_3 . The exothermic peak of phase modification of YBO_3 at around 600°C has already been observed by DTA during the first cooling. The consequent second heating has not shown any further exothermic formation peaks. Our XRD phase analysis showed also that YBO_3 phase formed completely during the first heating and neither B_2O_3 nor Y_2O_3 left in the sample.

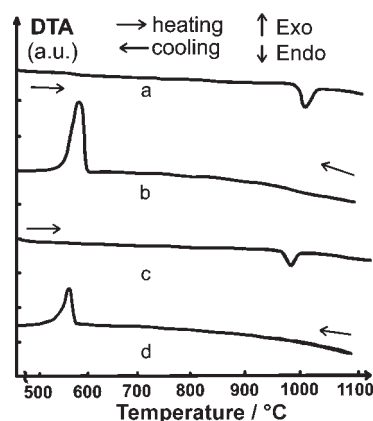


Fig. 1 Heating and cooling curves of YBO_3 prepared by sintering of $Y_2O_3:B_2O_3=1:1$ mixture at 1020°C, 10 h (curves a and b) and as formed from the same mixture in the DTA experiment ($10^\circ C\ min^{-1}$ heating rate, curves c and d). Natural cooling curve has been recorded

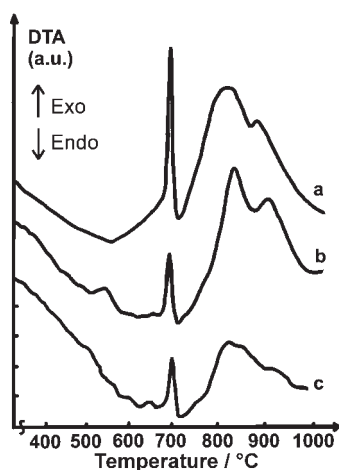


Fig. 2 Dominant exothermic heat effects of YBO_3 formation from mixture of Y_2O_3 and B_2O_3 when a – $Y_2O_3:B_2O_3=1:1$ molar ratio, (no third component present); b – $Al_2:B_2O_9$ added in $Y_2O_3:B_2O_3:Al_2O_3=1:4:3$ molar ratio; c – $Al_4B_2O_9$ added in $Y_2O_3:B_2O_3:Al_2O_3=2:5:3$ molar ratio

The addition of either Al_2O_3 or $\text{Al}_4\text{B}_2\text{O}_9$ to the above starting materials resulted in very similar DTA profile and formation of YBO_3 (Fig. 2, curves b and c). Nevertheless, a very small amount of $\text{YAl}_3(\text{BO}_3)_4$ (JCPDS 15-117) has also formed during DTA heating up to 1000°C , indicated by the single and weak appearance of its most intense X-ray diffraction peak.

Formation and thermal behavior of $\text{Al}_4\text{B}_2\text{O}_9$

In the Al_2O_3 – B_2O_3 system the borates, $\text{Al}_4\text{B}_2\text{O}_9$ and $\text{Al}_{18}\text{B}_4\text{O}_{33}$ are well-established compound phases [19]. Three files of X-ray diffraction reference of $\text{Al}_4\text{B}_2\text{O}_9$ can be found in ICDD (JCPDS) database [19, 20]. Pattern of the sample prepared by sintering a mixture of Al_2O_3 : B_2O_3 =2:1 at 1020°C for 30 h showed slight similarities to JCPDS files No. 9-158 and 29-10, but was quite different from file No. 47-319. The lattice distance – relative intensity values observed us are summarized in Table 1.

Table 1 Observed powder XRD data of $\text{Al}_4\text{B}_2\text{O}_9$

Lattice distance/Å	Relative intensity/%	Lattice distance/Å	Relative intensity/%
5.33	100	2.142	20
5.26	70	2.062	7
4.93	40	1.963	5
3.59	15	1.922	3
3.36	20	1.823	4
3.32	15	1.789	4
2.78	5	1.649	2
2.67	18	1.605	6
2.594	20	1.557	4
2.460	20	1.496	4
2.390	7	1.478	2
2.225	12	–	–

The same XRD pattern of $\text{Al}_4\text{B}_2\text{O}_9$ was even obtained in the DTA heating of oxide mixture with $10^\circ\text{C min}^{-1}$ rate up to 1050°C . The formation reaction was found exothermic between 900 and 1000°C (Fig. 3, curve b).

Peritectoid decomposition of $\text{Al}_4\text{B}_2\text{O}_9$ into $\text{Al}_{18}\text{B}_4\text{O}_{33}$ and B_2O_3 is reported to occur at 1035°C [21, 22]. Unfortunately, the expected heat effect of $\text{Al}_{18}\text{B}_4\text{O}_{33}$ phase formation could not be observed by DTA between 1000 and 1050°C using either oxide mixtures or sintered $\text{Al}_4\text{B}_2\text{O}_9$ phase (Fig. 3, curves a and b). $\text{Al}_{18}\text{B}_4\text{O}_{33}$ could only be prepared using higher temperature and longer time, finally we obtained it by sintering $\text{Al}_4\text{B}_2\text{O}_9$ at 1150°C for 10 h [13]. Its XRD pattern was in good agreement with all three reference patterns found in the ICDD database [23].

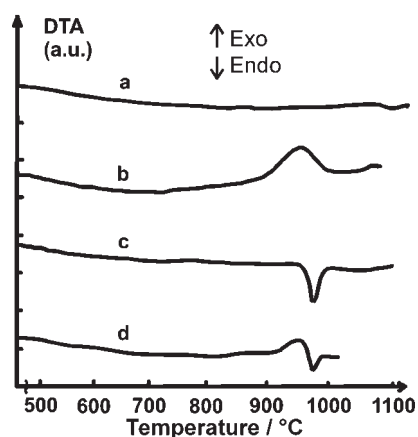


Fig. 3 DTA curves of a – $\text{Al}_4\text{B}_2\text{O}_9$ formed at 1020°C for 30 h; b – mixture of Al_2O_3 and B_2O_3 in 1:1 molar ratio; c – mixtures of YBO_3 and $\text{Al}_4\text{B}_2\text{O}_9$ in 4:3 molar ratio; d – mixture of YBO_3 , Al_2O_3 and B_2O_3 in 2:3:3 molar ratio

Formation and thermal stability of $\text{YAl}_3(\text{BO}_3)_4$

Unfortunately, no distinct and characteristic heat effect of $\text{YAl}_3(\text{BO}_3)_4$ could be observed by DTA up to 1050°C . The rate of solid state formation of YAB is probably slow on the used time scale of the DTA measurements below 1050°C , and resulted in only small amount of YAB. The most intense XRD peak of YAB was used to estimate the amount of this expected phase present.

We have compared the amounts of YAB formed in DTA experiments up to 1000 – 1050°C from the initial oxides (Fig. 2, curve b) with amounts obtained from various mixtures of oxides and borates (Fig. 2, curve c; Fig. 3, curve d and c) in order to check whether the usage of already-formed single borates (YBO_3 or $\text{Al}_4\text{B}_2\text{O}_9$ instead of simple oxides) facilitate the formation of the double borate, YAB. Although in each case, even in the DTA mixture of YBO_3 and $\text{Al}_4\text{B}_2\text{O}_9$ (Fig. 3, curve c) little amount of YAB has been formed below 1000°C , the ratio of $\text{YAl}_3(\text{BO}_3)_4$ was less than that formed from the initial oxide mixture. In each case at least one of the various thermal events with measurable heat effect occurred in the system (Figs 2 and 3, curves c and d) when the temporarily increased mobility of the particles of the solid lattices seems to be helpful for the nucleation of YAB phase, as well.

A considerable amount of YAB has been formed at $T=1150^\circ\text{C}$ sintering temperature for 10 h. A mixture of previously prepared YBO_3 and $\text{Al}_{18}\text{B}_4\text{O}_{33}$ (with some B_2O_3 also added) under the same circumstances was also very reactive. Meanwhile YAB has been formed, the $\text{Al}_{18}\text{B}_4\text{O}_{33}$ added has almost consumed. At room temperature some important lattice distances of the $\text{Al}_{18}\text{B}_4\text{O}_{33}$ phase are quite close to those of YAB (Table 2). If they remain still in coincidence at high temperature, then the conversion of the two phases may be facilitated by their epitaxial growth.

Table 2 Coinciding lattice distances of $\text{Al}_{18}\text{B}_4\text{O}_{33}$ and $\text{YAl}_3(\text{BO}_3)_4$

$\text{Al}_{18}\text{B}_4\text{O}_{33}$ (JCPDS 32-3) Lattice distance/Å	Relative intensity/ %	Orthorhombic indices s.g. No.63	$\text{YAl}_3(\text{BO}_3)_4$ (JCPDS 15-117) Lattice distance/Å	Relative intensity/ %	Rhombic indices s.g. R32
5.375	100	120	5.34	60	101
2.685	41	240	2.69	100	202

The decomposition temperature of YAB was reported to be 1235°C by Jung *et al.* [24]. $\alpha\text{-Al}_2\text{O}_3$, B_2O_3 , YAlO_3 , $\text{Al}_{18}\text{B}_4\text{O}_{33}$, Al_3BO_6 and AlBO_3 phases were detected as decomposition products after a heat treatment at 1300°C for 12 h [24]. As a result of long term (up to 30 days) heat treatment of $\text{Gd}_x\text{Y}_{(1-x)}\text{Al}_3(\text{BO}_3)_4$ ($x=0.6\text{--}0.75$) at 940–980°C formation of $\text{Al}_4\text{B}_2\text{O}_9$, $\text{Al}_{18}\text{B}_4\text{O}_{33}$ and RBO_3 ($R=\text{Y, Gd}$) phases were reported [11]. Sintering powdered YAB crystals at 1300°C for 2 h, we have identified only two phases, YBO_3 (JCPDS 16-277) and $\text{Al}_{18}\text{B}_4\text{O}_{33}$ (JCPDS 32-3) to be present and no YAB at all. These decomposition products formed probably according to the following equation:



The occurrence of the latter two borate phases during YAB decomposition is in harmony with the formation of YAB at 1150°C starting from the mixture of YBO_3 and $\text{Al}_{18}\text{B}_4\text{O}_{33}$. These two phases are probably the phases which are in equilibrium with YAB during its incongruent melting.

At higher temperatures the $\text{Al}_{18}\text{B}_4\text{O}_{33}$ phase is stable to 1440°C [19], while YBO_3 melts at around 1650°C [17].

Conclusions

In the $\text{Y}_2\text{O}_3\text{--B}_2\text{O}_3$ subsystem formation of YBO_3 has been observed, which has been accompanied with several exothermic heat effects between 700 and 1000°C not reported earlier. In the $\text{Al}_2\text{O}_3\text{--B}_2\text{O}_3$ subsystem an exothermic formation of $\text{Al}_4\text{B}_2\text{O}_9$ has been observed between 900 and 1000°C. The latter phase decomposed into $\text{Al}_{18}\text{B}_4\text{O}_{33}$ between 1050 and 1150°C. The *in situ* formation and conversion of single borate phases seems to facilitate the nucleation processes of YAB phase below 1050°C. Nevertheless, a considerable amount of YAB could be obtained during long term (10 h) sintering at 1150°C, when even the YBO_3 and $\text{Al}_{18}\text{B}_4\text{O}_{33}$ phases have reacted with each other in the presence of B_2O_3 . Peritectoid decomposition products of YAB from 1300°C were also the phases of YBO_3 and $\text{Al}_{18}\text{B}_4\text{O}_{33}$.

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