THERMAL STUDY ON Li BIS(OXALATEBORATE) LiBOB

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ABSTRACT. The thermal stability of the lithium bis(oxalatoborate) (LiBOB) in the temperature range of 40 to 350 ºC was studied by accelerating rate calorimetry (ARC), differential scanning calorimetry (DSC) and thermal gravimetric analysis. An endothermic reaction was detected with an onset at ~ 293 ºC involving a complete irreversible decomposition of the LiBOB in which gaseous products are formed. In the first stage $Li_2C_2O_4$ (crystalline), B_2O_3 (glass), CO and CO_2 gases are formed. The next stage is an irreversible formation of lithium triborate LiB_3O_5 (glass).

Introduction

The new lithium salt bis(oxalatoborate) was recently proposed by Lishka *et al.*[1] and Xu and Angell [2] as a very promising and advantageous electrolyte for rechargeable Li ion batteries, instead of the problematic $LiPF_6$ which is the commonly used Li salt in the electrolyte solutions for commercial Li ion batteries.

During the last ten years, a number of papers appeared in the literature, demonstrating good performance of graphite anodes and transition metal cathodes in solution containing LiBOB (compared to the behavior in solutions based on the commonly used salt $LiPF_6$). It was also demonstrated that the thermal stability of electrolyte solutions based on LiBOB for Li ion batteries, is much higher compared to systems based on other Li salts (e.g. $LiPF_6$, $LiBF_4$).[3] Hence, it is clear that the intrinsic thermal behavior of LiBOB is interesting and important in connection to R & D of novel and safer Li ion batteries. Indeed, in recent years, some reports on thermal studies of LiBOB appeared, as summarized below. According to thermogravimetric experiments, lithium-bis(oxalatoborate) is fully stable up to approximately 300 ºC [1]. Differential thermal analysis combined with thermogravimetric analysis (DTA-TGA) using a scanning rate of 10 ºC min^{-1}, showed that LiBOB is stable up to 302 ºC. Beyond this temperature, it decomposes rather than melts [2]. This salt is chemically stable in organic solutions but it slowly decomposes by hydrolysis to $LiBO_2$ and LiOOCCOOH [2]. Amine *et al.*[4] presented thermogravimetric curve for LiBOB in the temperature range 20 to 600 ºC. Bi-Tao Yu [5] reported about the stability of LiBOB in the temperature range 240-300 ºC, and about LiBOB decomposition to Li_2CO_3, B_2O_3, CO_2 and CO when the temperature is higher than 300 ºC. They observed a weight loss related to two processes at temperatures about 320 ºC and 450 ºC. It was reported that the decomposition of LiBOB at 302 ºC produces B_2O_3 and CO_2 [6].

Despite of the intensive studies of LiBOB and its solutions on both electrochemical performance and thermal behavior, there is not yet a comprehensive picture of the intrinsic thermal behavior of this salt and a clear analysis of all the products of its thermal reactions. Therefore, the present work aims at providing a better and more complete picture of the thermal behavior of LiBOB including a rigorous analysis of its decomposition products, and a comprehensive understanding of its calorimetric response.

Experimental

Highly pure LiBOB salt was obtained from Chemetall Inc. and could be used as received. The pristine salt and its thermal dissociation products were characterized by Fourier transform infrared (FTIR) spectroscopy, (Magna 860 Spectrometer from Nicolet Inc., placed in a glove box under H_2O and CO_2-free atmosphere), element analysis by an inductively coupled plasma (ICP) spectrometer (Ultima 2, Jobon Yvon Horiba), optical microscope (AX70/AX70A, Olympus Inc.), scanning electron microscopy (SEM) (JEOL JSM 840), and X-ray diffraction using a D8 Advance System from Brucker Inc. XRD patterns were obtained using Cu K_α radiation (λ=1.54Å) at 40 mA and 40 kV. We used the cell which enabled the isolation of the sensitive samples from atmospheric gases by polyester Mylar type film 90 μ thick transparent for X-ray radiation. An accelerating rate calorimeter (ARC) from Arthur D Little Inc., Model 2000, a differential scanning calorimeter (DSC) from Mettler Toledo Inc., Model DSC 822, and thermogravimetry (TG, DTA) (SDT 2960, TA instrument) were used for the thermal analysis of LiBOB.

In the ARC measurements, about 1 gram of salt was loaded in a titanium flask (8.2 ml volume) in an argon filled glove box (VAC Inc.) and was transferred to the ARC under purified Ar atmosphere The salt was heated from 40 to 300 ºC in 5 ºC increments at the rate of 2 ºC min^{-1} in the search for self-heating at a sensitivity threshold of 0.02 ºC min^{-1}. The controller was programmed to wait 15 min for the sample and the calorimeter temperatures to equilibrate, and then to search during 20 min for a temperature increase of 0.02 ºC min^{-1}. After the ARC experiments, the reaction vessel (a titanium flask) was cooled with liquid nitrogen until the pressure was close to the atmospheric pressure. The gaseous products were released through a specially designed high-pressure valve. For NMR analysis the gas was collected into CD_3CN solution.

TGA-DTA measurements were conducted under pure nitrogen atmosphere in alumina crucibles, 70 μl in volume.

DSC measurements in confined volume were conducted in hermetically sealed, gold-plated stainless steel crucibles 30 μl in volume (Mettler Toledo Inc.), over a temperature range of 40– 350 ºC. The crucibles were filled with about 10 mg of the salt, and then sealed in a glove box under an argon atmosphere. The heating/cooling rates were 0.5, 1 and 20 ºC min^{-1}.

Results

The significant pressure increase during ARC experiment at an onset of 265ºC and the negative slop in the temperature steps appearing at about 268 ºC, may be explained by an endothermic decomposition of LiBOB. The gaseous products of this reaction were collected and analyzed (see later).

Figure 1 presents TGA and DTA curves, related to heating LiBOB and Li oxalate samples. This figure, related to LiBOB, shows two endothermic peaks at about 100 ºC and 310 ºC, respectively, in the DTA curve, accompanied by a weight loss. The first endotherm is attributed to the loss of adsorbed water. The water content in the samples is near 0.06 % according to the TGA results (Fig. 1). The second endotherm with an onset at about 293 ºC (Fig. 1) is related to LiBOB decomposition. The weight loss calculated after the process completion, based on the TGA and the ARC measurements, is 61.2±0.5 %.

Fig. 2 shows typical DSC curves obtained from LiBOB (a, b, c) and mixtures of B_2O_3-Li oxalate (d) in closed crucibles. One endothermic irreversible process is distinguished in the temperature range 210 to 390 °C (Fig. 2a). It associates with

LiBOB decomposition. The onset of the endothermic dissociation of LiBOB is fixed at about 293 °C. The decomposition heat is about 38 kJmol^{-1} (196 Jg^{-1}).

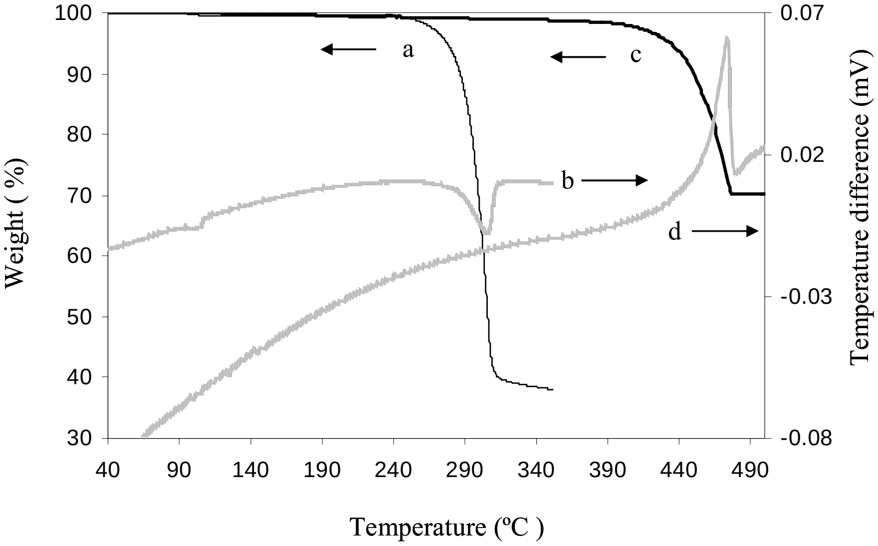


Fig. 1. TGA (a, c) and DTA (b, d) curves obtained by heating LiBOB samples at rate of 1 °C min^{-1} (14.830 mg) (a, b), and Li oxalate (5.255 mg) (c, d).

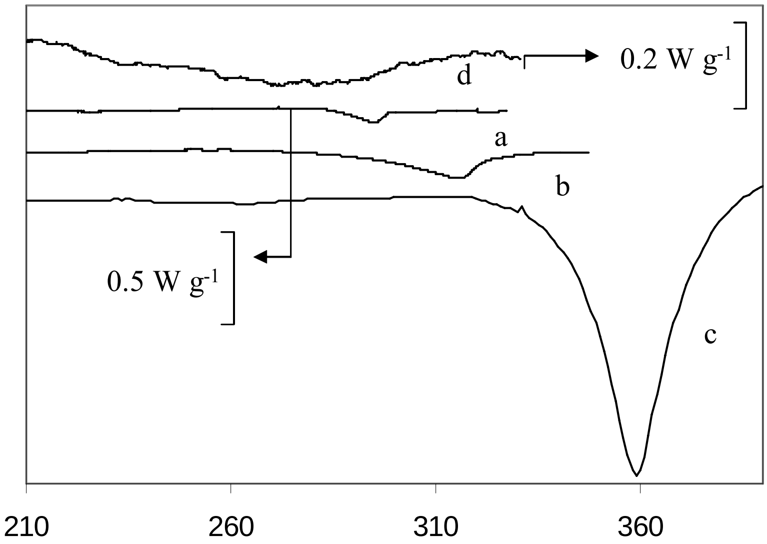
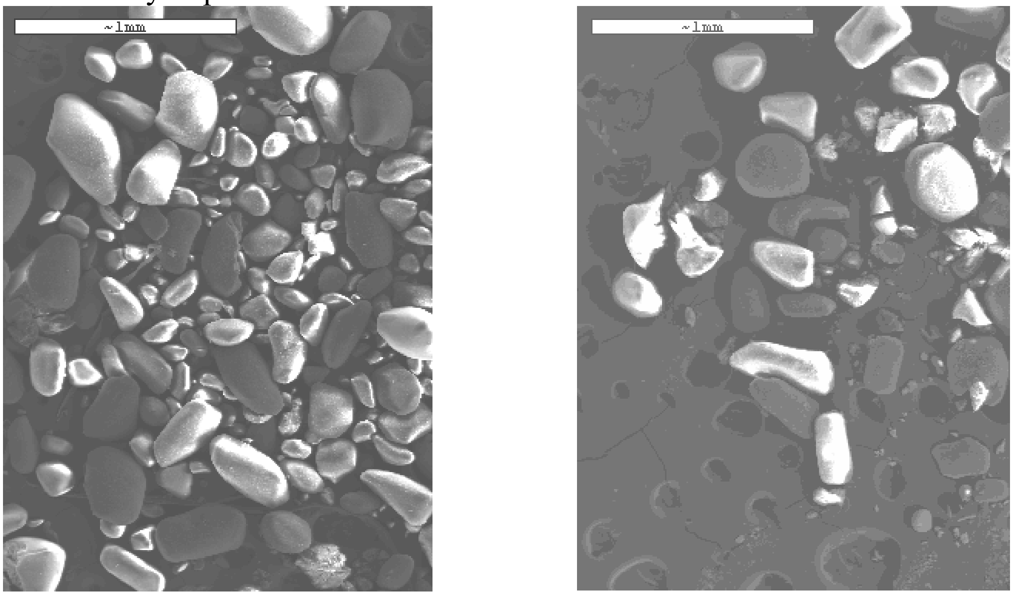


Fig. 2. DSC curves obtained by heating LiBOB samples of different weights (indicated) at different heating /cooling rates (indicated): (a) 0.5 °C min^{-1}, 2.789 mg, (b) 1 °C min^{-1}, 8.037 mg, (c) 20 °C min^{-1}, 3.434 mg, and (d) $Li_2C_2O_4$-B_2O_3 mixture sample (1.717 mg) heated at a rate of 1°C min^{-1}.

Fig. 2 (a, b, c) shows typical DSC curves at different heating/cooling rates. These results provide further as evidence for the endothermic reaction of LiBOB rather than phase transition. The onset and peak temperatures of the endotherm shift to higher values as the heating rate is higher (Fig. 2). This behavior is typical for chemical processes, rather than to phase transition. The shape of the peak does not change at higher rates, and no indication for the existence of an accompanying process is observed.

Figure 2d showing the thermal behavior of B_2O_3-Li oxalate mixture reflects an endothermic reaction between these two species at the same temperature range as that

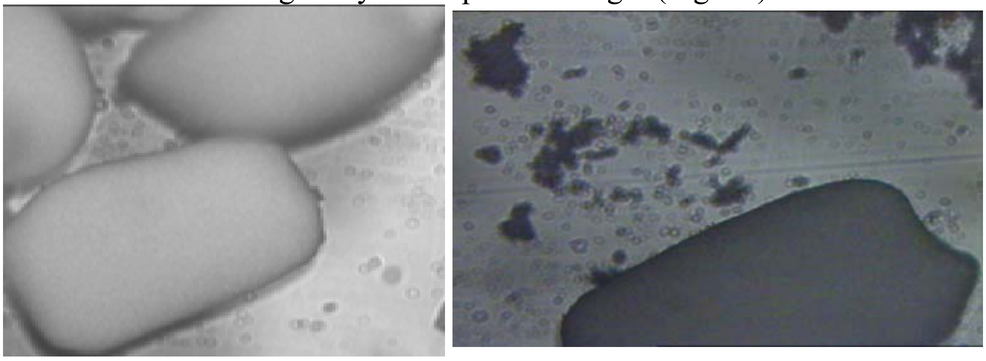
LiBOB decomposition with a reaction heat around 67.9 kJ per mole of reacting B_2O_3. This data is very important for the discussion see later.



a b

Fig. 3. SEM micrographs of: (a) pristine LiBOB samples; (b) LiBOB after heating to 350 °C. A scale appears in each micrograph.

Figs. 3, 4 show SEM and optical micrographs of pristine and heated LiBOB powder. The pristine white powder consists of elongated round particles with 0.1-0.5 mm length and 0.05-0.25 mm diameter. Surprisingly, the particles' shape and size did not change noticeably after heating to 350 °C (Figs. 3a and 3b) in spite of the loss of weight of about 60 %. They are non transparent under transmitted light (Fig. 4a) and don't demonstrate non homogeneity under polarized light (Fig. 4b).



a b

Fig. 4. Photomicrographs from optical microscope of the powder obtained after heating of LiBOB samples to 350 °C: **(a)** transmitted light (x 10); **(b)** polarized light (x 5).

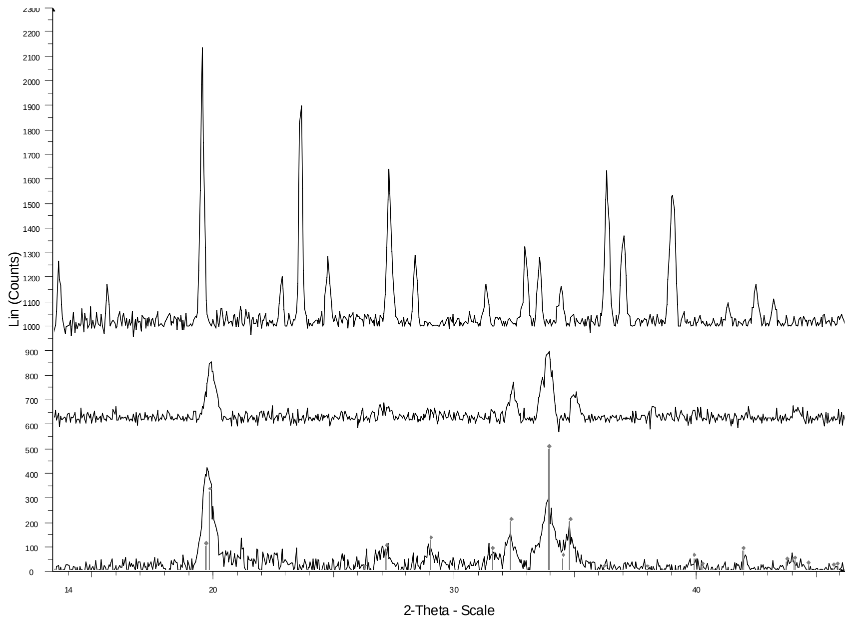


Fig. 5. XRD patterns of: (a) a pristine LiBOB powder, (b) a powder obtained by heating LiBOB to 350 °C, **(c)** same as (b) after storage at 300 °C during 10 days. Line marks of Li oxalate are shown for comparison.

Fig. 5 shows XRD patterns of the pristine salt and the solid decomposition product (collected after heating). The XRD patterns of the pristine LiBOB correlates well with literature data [7]. No observation of pristine LiBOB peaks after heating to 350 °C indicates a complete LiBOB decomposition. Three powders, after heating in closed volume in ARC bomb, in DSC crucibles, and in opened alumina crucibles in TGA tests, show identical XRD patterns. All peaks correspond to monoclinic lithium oxalate[8]. A further storing of this product during 10 days at 300 °C did not caused any structural changes (confirmed by XRD and SEM).

There is a good agreement between the XRD measurements and the FTIR spectra (Fig. 6). As seen in Figure 6, the IR bands of LiBOB pristine are not detected after heating to 350 °C but all the expected IR peaks of Li oxalate can be seen in the spectra of the thermal product.

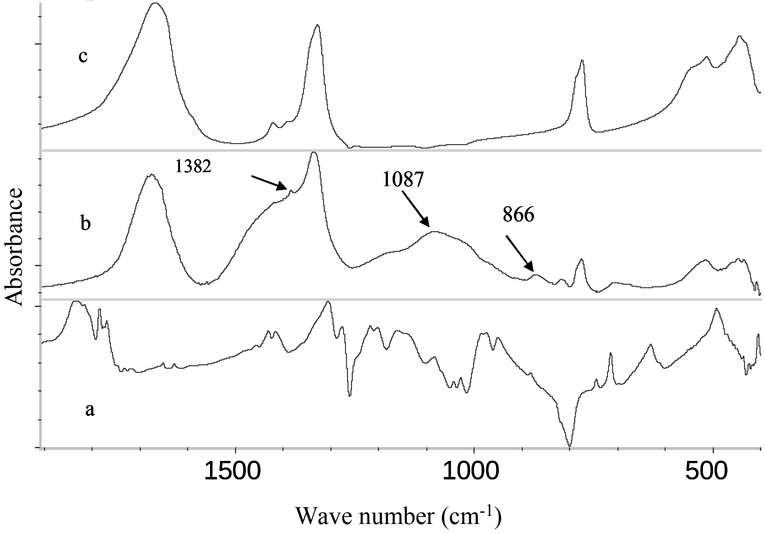


Fig. 6. FTIR spectra of: (a) pristine LiBOB powder, (b) the powder obtained by heating LiBOB heating to 350 °C, and **(c)** Li oxalate powder.

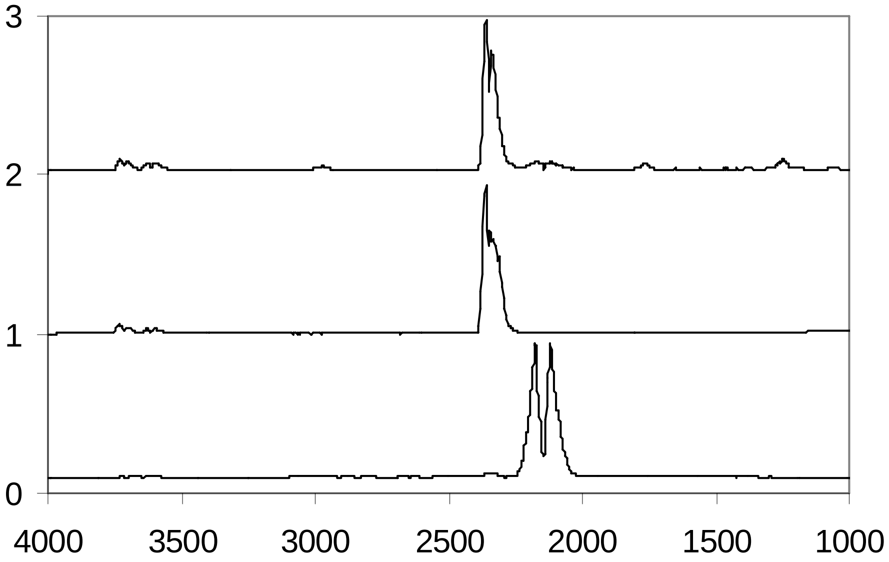


Fig. 7. FTIR spectrum of gas phase that is formed in the ARC calorimetric bomb due to a thermal decomposition of LiBOB (a). Spectra of CO_2 (b) and CO (c) are presented for comparison.

Figure 7 compares FTIR spectra of the gaseous product of LiBOB thermal decomposition to spectra of CO_2 and CO. From these studies, it is clear that the gaseous product of LiBOB decomposition comprises both CO_2 and CO. The final solid product of the LiBOB thermal decomposition was dissolved in acidic solution and was analyzed by ICP. From this analysis it was found that the solid end product contains 9.3% Li and 13.9% B.

Discussion

Based on the above mentioned results the following mechanism of LiBOB decomposition at ~ 300 °C may be suggested:

$$2LiBC_4O_8(cryst) \rightarrow Li_2C_2O_4(cryst) + B_2O_3(glass) + 3CO(gas) + 3CO_2(gas); \qquad (1)$$

$$Li_2C_2O_4(cryst) + 3B_2O_3(glass) \rightarrow 2LiB_3O_5(glass) + CO(gas) + CO_2(gas); \qquad (2)$$

The overall thermal l decomposition process of LiBOB is:

$$3LiBC_4O_8(cryst) \rightarrow Li_2C_2O_4(cryst) + LiB_3O_5(glass) + 5CO(gas) + 5CO_2(gas) \qquad (3)$$

The calculated weight loss due to a complete decomposition of LiBOB according to equation 1 is 55.7 %. However the TGA and the ARC experiments showed higher weight loosed due to the thermal decomposition processes. The weight loss demonstrated in the TGA data (Fig. 1) is near 62 %. The further exposure of the samples to air at room temperature, after heating to 350 °C, did not cause any further change in mass during 24 hours. Nevertheless, it is known that boron oxide reacts slowly with water to form boric acid. FTIR spectra of the LiBOB samples after heating to 350 °C indicated the absence of B_2O_3 as a final decomposition product (Fig. 6).

Hence, an additional process with gas evolution is needed to explain a weight loss around 62%. This second (to equation 1) process cannot be a partial decomposition of lithium oxalate, because it decomposes to carbonate only near 500 °C according to our TGA-DTA measurements (Fig. 1) and literature data [9]. Hence, we suggest reaction 2 above as a follow up process that very well explains weight loss measured herein.

As suggested by equation 2, all the B_2O_3 produced by the first process (eq. 1) is consumed by the second step. In this follow up reaction, only 1/3 of the Li oxalate formed by the first process is consumed. This correlates well with the fact that the final products of LiBOB decomposition contain Li oxalate, as evidenced by both XRD and FTIR measurements (Figs. 5, 6). The overall processes, described by equation 3, suggest a loss of mass of about 61.6% (compared to the initial mass of LiBOB) due to the formation of CO and CO_2. This correlates very well with the experimental results (DTA-TGA, Fig. 1) that show a mass loss of about 62% when LiBOB thermally decomposes. Li triborate, LiB_3O_5, is formed as a non crystalline glass phase and cannot be identified by X-ray diffraction. Fig. 6 presents FTIR spectra of pristine LiBOB and of a sample after heating to 350 °C, and of Li oxalate for comparison. The spectrum of the decomposed sample clearly shows Li oxalate bands at 449, 516, 775, 1330, and 1665 cm^{-1}, and three new bands, at 1087, 1382 and 866 cm^{-1} (not related to Li oxalate). These peaks can be assigned indeed to the strong bands of LiB_3O_5 at 1372, 1087 and 860 cm^{-1} [10]. The composition of the end solid product after heating LiBOB to 623 K according to the ICP analysis (9.3 % Li and 13.9 % B) correlates well with the solid product suggested by equation 3 above, namely, a mixture of $Li_2C_2O_4$+LiB_3O_5 (9.4 % Li and 14.5 % B).

We checked the possibility of the reaction suggested by equation 2 by DSC measurements. Mixtures containing $Li_2C_2O_4$:B_2O_3 1:3 mol/mol were thoroughly grinded in agate mortar and pestle and then were measured by DSC in closed crucibles up to 500 °C. A pronounced broad endothermic peak appears in the same temperature range in which LiBOB decomposes (Fig. 2). The onset of this peak is near 210 °C that is by 80 °C lower than the onset of the LiBOB decomposition peak (eq. 1). The heat of the endothermic reaction between Li oxalate and B_2O_3 is about 67.9 kJ per mol of the product LiB_3O_5 as measured herein. According to equation (3) only 1/3 mol of LiB_3O_5 is formed by decomposition of 1 mole of LiBOB. Therefore, about 67.9/3~23 kJ per mole of LiBOB is absorbed for formation of 1/3 mol of LiB_3O_5. This value is part of the heat of LiBOB decomposition, about 38 kJ mol^{-1}. Consequently, the heat of the first decomposition step of LiBOB, equation (1), is near 38-23=15 kJ mol^{-1}. XRD measurements of the product of heating the $Li_2C_2O_4$-B_2O_3 mixture (up to 350 °C) showed no evidence of a crystalline phase. The temperature of the endotherm related to the reaction of Li oxalate and B_2O_3 is too low for the oxalate decomposition. Therefore this process can be related only to the reaction 2. Hence, reaction 2 begins immediately when $Li_2C_2O_4$ and B_2O_3 appear as a result of LiBOB decomposition (eq. 1).

In order to complete the discussion, it is important to mention that the element analysis of the final solid product of LIBOB decomposition which showed 9.3% Li and 13.9% B can not be unambiguously related only to a mixture of $Li_2C_2O_4$-B_2O_3 1:1.

One may suggest that such an atomic ratio may relate also to the following mixture: $Li_2O\cdot 2B_2O_3$ ($Li_2B_4O_7$)+$Li_2O\cdot 4B_2O_3$ ($Li_2B_8O_{13}$) instead of LiB_3O_5. However, such a mixture containing 75% B_2O_3 should undergo a slow crystallization upon storage at elevated temperatures[11]. The end product of the LiBOB decomposition was stored at 300 °C during 10 days followed by XRD measurements. (This is the highest temperature in which a mixture containing Li oxalate can be heated and remain stable). No evidence for the formation of any new crystalline phase except the existing Li oxalate was observed by X-ray diffraction after storage at elevated temperatures (Fig. 5c).

Conclusion

The results of ARC, DSC and TGA experiments and their comprehensive analysis demonstrate the complete irreversibility of the endothermic decomposition of LiBOB under conditions of constant and open volume. The onset of decomposition is fixed at 293±4 °C; heat of decomposition is 37.8±3.1kJ mol^{-1}.

Decomposition commences with formation of Li oxalate (crystalline) and boron oxide in the first step. The endothermic reaction between $Li_2C_2O_4$ and B_2O_3 results in the second step the formation of LiB_3O_5 as glass material. These two steps are accompanied by the development of CO and CO_2.

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