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A thermogravimetric analysis study of volatilization of flux mixtures used in XRF sample preparation†

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This paper deals with the thermal behaviour occurring during the formation of lithium borate glasses. Thermogravimetric analysis and differential scanning calorimetry were employed to identify reactions occurring during fusion in pure flux mixtures. The conditions around the identified reactions were reproduced in a muffle furnace to obtain larger quantities of material for further investigation using spectroscopic techniques. It was shown that above 1050 °C lithium borate fluxes volatilize, which could lead to inaccurate analytical results. Copyright © 2004 John Wiley & Sons, Ltd.

INTRODUCTION

The fused glass bead sample preparation method for XRF spectrometry was introduced in 1957 by Claisse,[1] and soon became the preferred method for introducing oxide samples into the spectrometer, because mineralogical and particle size effects are eliminated during the fusion process and matrix effects are largely reduced by the resulting dilution.[2–5] With the recent advances in XRF spectrometers, spectroscopists today have at their disposal instruments with enhanced generator and temperature stability, high sensitivity even for light elements and effective matrix correction software. Consequently, the largest proportion of analytical error originates during the sample preparation step. Even after 45 years of using fused beads for XRF analysis, certain matrices still prove to be problematic. Although a number of reports on fusion methods for chromite-, sulphide- and cassiterite-rich materials have been published,[6,7] routine methods for these are still eluding analytical chemists. Lengthy fusion steps at temperatures in excess of 1100 °C are often stipulated[6,8] for refractory materials and ores.

It appears that the reactions occurring in a sample–flux mixture during the fusion process have not been addressed. It is also not possible to evaluate the role of temperature fluctuations in modern automatic fluxers with gas burners. As part of a systematic programme to evaluate the interactions between geological samples and different fluxes during fusion, the volatilization of commercial fluxes was studied.

In this study, the conditions prevailing in a crucible with a flux mixture were simulated with a thermogravimetric analyser and pure flux mixtures as a baseline.

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EXPERIMENTAL

For most silicate and oxide matrices, lithium tetraborate ($Li_2B_4O_7$), lithium metaborate ($LiBO_2$) or mixtures in different ratios are used as flux. A range of these different composition mixtures, from different commercial sources and thus manufacturing methods, were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), using a Netzsch STA 409 EP simultaneous thermal analyser. Between 20 and 40 mg of the flux were analysed in a platinum crucible using a heating rate of 10 °C min^{-1} over the range 20–1280 °C. The TGA curve indicates the percentage weight loss as a function of increasing temperature, and the DSC curve measures the energy changes in the samples, by comparing the heat with the temperature change between an empty reference crucible and the crucible containing the sample, expressed in μV. A positive signal indicates an exothermic reaction and a negative signal indicates an endothermic reaction.

RESULTS AND DISCUSSION

Three pure lithium tetraborate samples were evaluated (Figs 1–3). Below the melting-point of lithium tetraborate (920 °C), the TGA curve is constant around 0%. Some initial weight losses around 200 °C can be ascribed to the loss of adsorbed water. Lithium borates are known to be hygroscopic. The content of adsorbed water was lowest in the flux from source A, which is a pre-fused flux. The advantages of a fusion step in the manufacturing process are the elimination of residual volatiles and an increase in density and particle size, with a resulting decrease in the surface area exposed to the atmosphere. The endothermic reaction on the DSC curve at 920 °C corresponds to the theoretical melting range of lithium tetraborate (920–930 °C). During the 18 min of heating from 1020 to 1200 °C, between 2 and 6% weight loss was observed in the samples. The largest weight loss was in source B (Fig. 2), which was not pre-fused during the manufacturing process. At ~1020 °C, a sudden decrease in

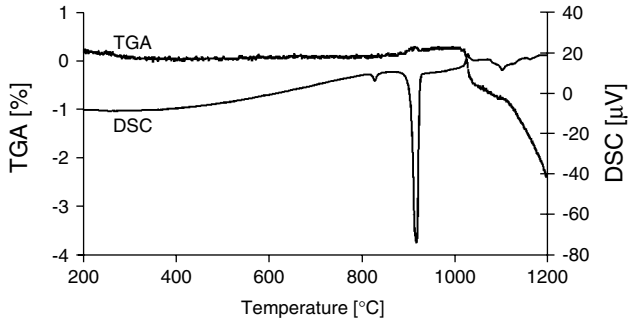

Figure 1. TGA and DSC curves for lithium tetraborate: source A.

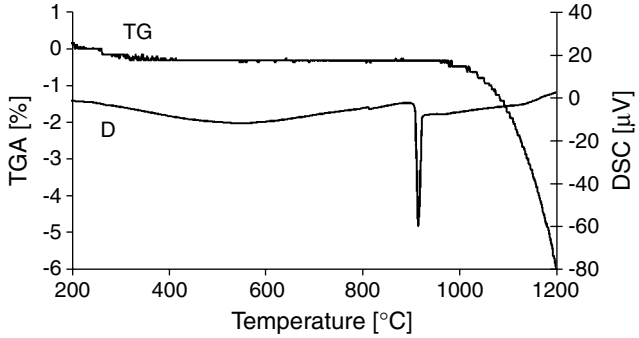

Figure 2. TGA and DSC curves for lithium tetraborate: source B.

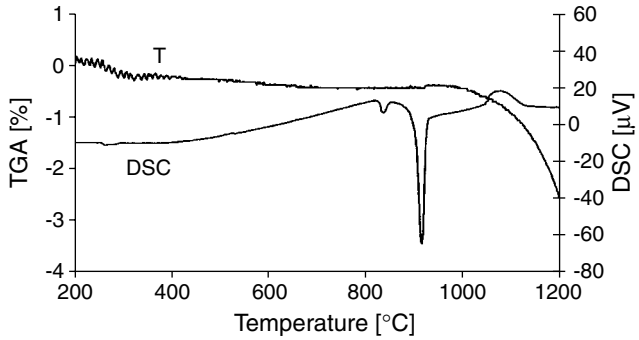

Figure 3. TGA and DSC curves for lithium tetraborate: source C.

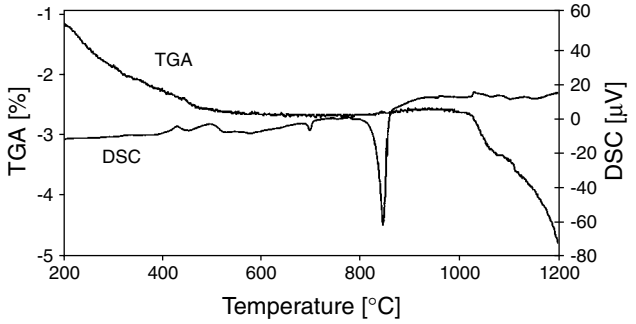

Figure 4. TGA and DSC curves for lithium metaborate: source A.

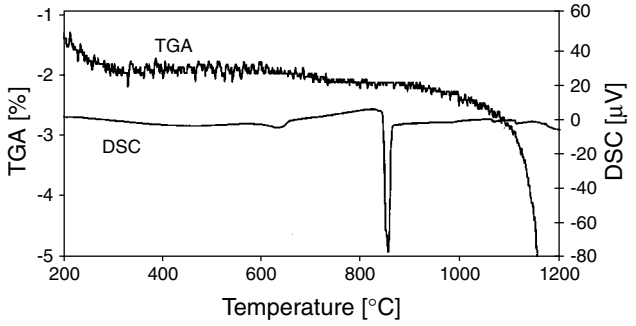

Figure 5. TGA and DSC curves for lithium metaborate: source B.

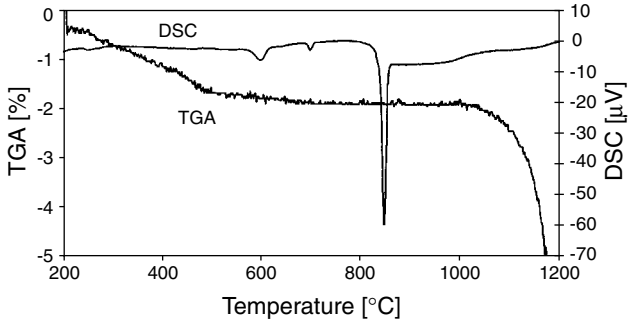

Figure 6. TGA and DSC curves for lithium metaborate: source C.

the TGA curve is observed, corresponding to an exothermic reaction on the DSC curve. This observation is most marked in the flux from source A. This loss of flux is described in more detail later.

Three pure lithium metaborate samples were evaluated (Figs 4–6). The comparatively large weight loss below 500 °C can be ascribed to the hygroscopic nature of lithium metaborate. This increase in hydrophilic group per unit mass of lithium metaborate compared with lithium tetraborate is one of the reasons why lithium metaborate is seldom used on its own as a flux for XRF sample preparation, although the melting-point is lower than that of lithium tetraborate. This latter characteristic is an advantage when preparing a sample solution to be analysed by inductively coupled plasma (ICP) and atomic absorption spectrometric analysis. From 500 °C to the melting-point (corresponding to the theoretical melting-point at 845 °C), the TG curve is stable and, as in the case of lithium tetraborate, a 2–3% weight loss was observed between 1020 and 1200 °C. Source A (Fig. 4) was the only sample in which the TG loss corresponded to a small exothermic event on the DSC curve. The manufacturing process of this sample included a pre-fusion step.

Five commercially available mixtures were evaluated. (Figs 7–11). Melting-points for the individual mixtures are easy to identify by the endothermic reaction on the DSC curves. For compositions with more than 50% lithium metaborate, the melting temperatures are in the same range as for pure lithium metaborate (Figs 7 and 10), around 845 °C. For compositions with more $Li_2B_4O_7$ than $LiBO_2$, dual melting-points were observed, at 845 °C and a smaller melting reaction at 900 °C (Figs 8 and 11). Both of these flux mixtures were pre-fused during the manufacturing process, which indicates that different lithium borate species might co-exist even after fusion, although not pure lithium tetraborate and lithium metaborate. It was only for the 50 : 50

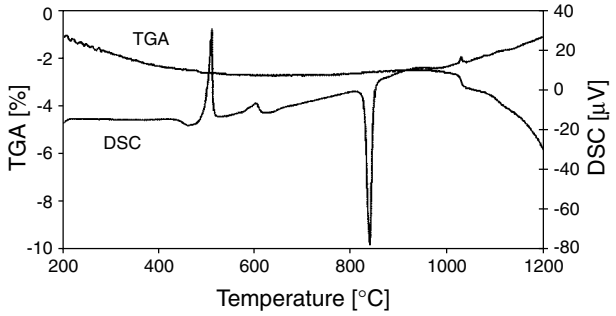

Figure 7. TGA and DSC curves for 20%$Li_2B_4O_7$–80%$LiBO_2$: source A.

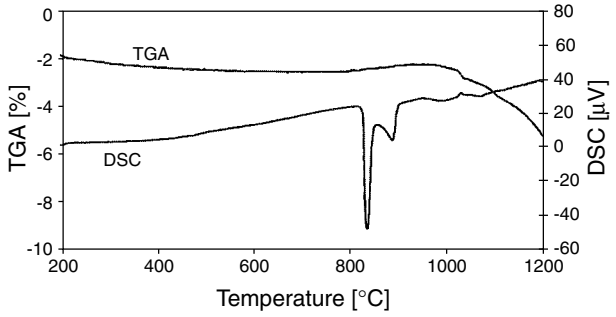

Figure 8. TGA and DSC curves for 66%$Li_2B_4O_7$–34%$LiBO_2$: source A.

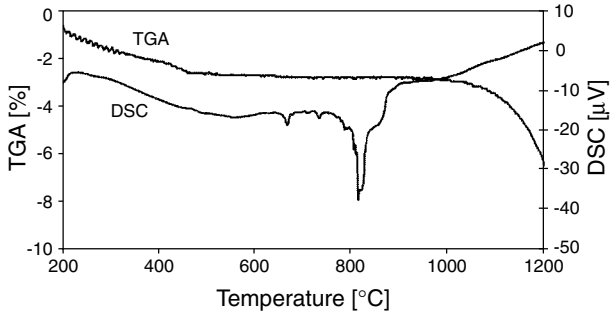

Figure 9. TGA and DSC curves for 50%$Li_2B_4O_7$–50%$LiBO_2$: source C.

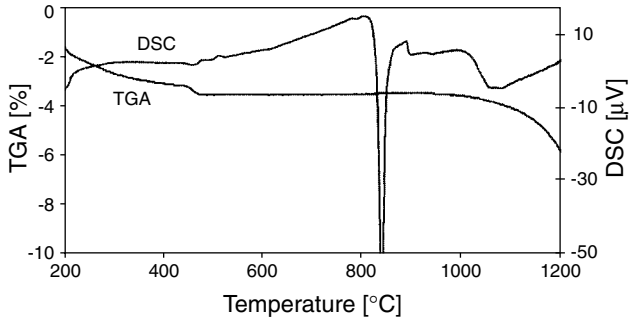

Figure 10. TGA and DSC curves for 35%$Li_2B_4O_7$–65%$LiBO_2$: source D.

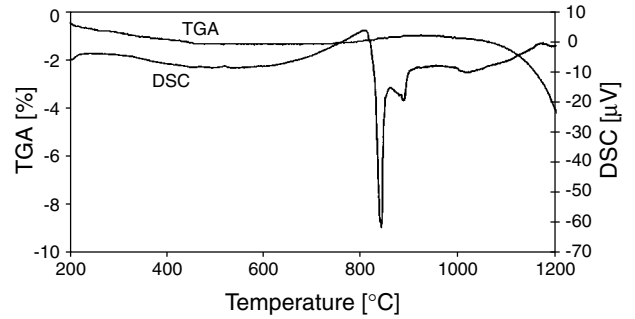

Figure 11. TGA and DSC curves for 57%$Li_2B_4O_7$–43%$LiBO_2$: source D.

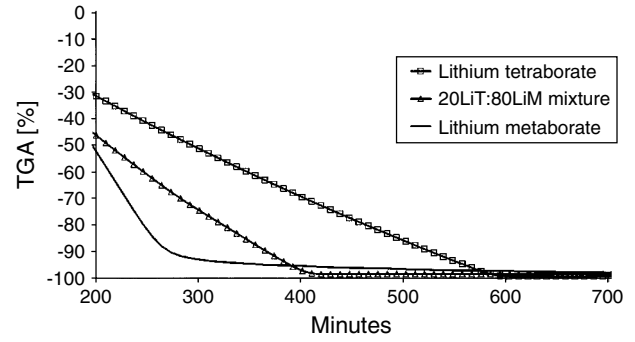

Figure 12. TGA curves for 900 min at 1230 °C.

mixture (Fig. 9) that a single, different melting temperature, a eutectic around 800 °C, was observed. Above 1020 °C, a weight loss of more than 2% was observed for all the compositions.

For practical application, it is of paramount importance to know whether this observed weight loss reaches equilibrium during the time required for fusing. Portions of lithium tetraborate, lithium metaborate and a 20 : 80 mixture were heated to 1230 °C and monitored by TGA analysis under isothermal conditions (Fig. 12). For previous TGA work, the heating curve was programmed from 20 to 1280 °C,

Table 1. ICP analysis on flux mixtures

		12 h at 1000 °C		12 h at 1150 °C		
Flux:	Parameter	B (%)	Li (%)	B (%)	Li (%)	LOI (%)[a]
Lithium tetraborate	Analysed concentration	25.0	6.9	24.4	6.7	2.17
	Theoretical value	25.57	8.21			
Lithium metaborate	Analysed concentration	21.5	12.4	20.6	12.0	2.19
	Theoretical value	21.73	13.95			
20 : 80 mixture	Analysed concentration	22.3	11.2	22.0	11.0	1.60
	Theoretical value	22.50	12.80			

[a] Determined gravimetrically.

but measurements were only recorded between 200 and 1200 °C because the accuracy of measurements decreases as the heating curve's upper limit is approached. For the isothermic measurements, 1280 °C was also set as the upper limit, but recordings were made at 1230 °C for the same reason. It was found that all flux had evaporated after a period varying from 350 min for lithium metaborate, 400 min for the mixture and 600 min for lithium tetraborate.

The gradual loss of flux could imply that the flux was evaporating, or dissociating, i.e. components were lost preferentially. To investigate this further, 5 g portions of lithium tetraborate, lithium metaborate and a 20 : 80 mixture were dried and tempered in a muffle furnace at 1000 °C for 12 h. A second portion of each was heated at 1150 °C for 12 h. The samples were subsequently dissolved in 25% HCI and analysed on a Varian Liberty 220 ICP analyser for lithium and boron.

Neither boron nor lithium analyses agreed with the theoretical compositions listed (columns 3 and 4, Table 1). This is probably more indicative of the limitation of the analytical technique for the stated elements than the sample purity, as certified ultrapure fluxes were used in the investigation. When considering the boron: lithium ratios, 3.6 for lithium tetraborate (theoretical 3.1), 1.7 for lithium metaborate (theoretical 1.6) and 2.0 for the 20 : 80 mixture (theoretical 1.8), it was found that the lithium and boron levels decreased at a constant rate, which indicates that the loss on ignition (LOI) is a volatilization reaction rather than a dissociation of the constituents.

CONCLUSIONS

It is strongly recommended that fusion temperatures for lithium borate fluxes do not exceed 1050 °C. Higher temperatures (e.g. 1230 °C) inevitably lead to the loss of flux. Depending on the flux type, such volatilization was found to vary from 2 to 6% per hour (Fig. 12). The effects of network formers such as SiO_2 or network modifiers such as Mg, Na and K on this volatilization will have to be evaluated as the presence of more network formers will probably stabilize the melt structure, increase the viscosity and decrease volatilization. The danger lies in fusing difficult to dissolve materials for long times at elevated temperatures.

Constant rates of volatilization, which have to be evaluated for every flux type, can be accommodated in laboratory sample preparation techniques if time schemes for the fusion steps are strictly adhered to and temperatures of fusion are rigorously controlled.

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