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DETERMINATION OF THE RHOMBIC TO CUBIC TRANSITION TEMPERATURE OF THE ALKALI METAL TETRAFLUOROBORATES USING DIFFERENTIAL THERMAL ANALYSIS*

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ABSTRACT

A systematic investigation of the rhombic-to-cubic transition temperatures of the alkali metal tetrafluoroborates using differential thermal analysis (DTA) is reported. This transition has previously been reported on $NaBF_4$ and KBF_4, both measured by X-ray diffraction techniques more than twenty years ago, without independent confirmation. No literature references to the measurement of this transition temperature were found for the other three compounds.

INTRODUCTION

In 1936, the rhombic–cubic transition temperatures for $NaBF_4$ and KBF_4 were reported by Finbak and Hassel[3], using X-ray diffraction techniques. No further investigations of this series have been found in the literature. Gordon and Campbell[2] found that differential thermal analysis (DTA) yielded transition temperature data for the isomorphous perchlorates. Their report suggested a method to determine the rhombic–cubic transition temperatures of the tetrafluoroborate salts of Li, Na, K, Rb, and Cs. Transition-temperature values were determined by DTA using a standard commercial instrument. The observed endotherms are sharp, reproducible, and readily obtained. The effects of furnace atmosphere, composition of system components, and heating rates are discussed.

This work is a continued investigation based on a thermal study of KBF_4 reported by the authors in 1968[1]. In this investigation a large, sharp endothermic peak was observed at the known rhombic–cubic transition temperatures of this salt.

Of the five compounds in the series, only two of these salts were found to have been reported at all, and those were studied by X-ray diffraction. The transition temperatures for $NaBF_4$ and KBF_4 were determined by Finbak and Hassel in 1936, who reported transitions for $NaBF_4$ at 298.2 °C and for KBF_4 at 278.7 °C.

EXPERIMENTAL PROCEDURE

The study was performed using a standard commercial thermal analyzer

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manufactured by Fisher Scientific Company including the Fisher Model 360 Linear Temperature Programmer and the Model 260 furnace. The thermograms were recorded on a Texas Instrument two pen strip chart recorder with 1-mV full scale response. The sample holder was an Inconel cylinder with eight symmetrically arranged round holes. The sample was placed in a graphite crucible which in turn was placed in the sample holder. The differential thermocouple was then inserted into the sample and reference, and the holder, crucibles, thermocouples, and sample placed in the furnace. The lead cable from the furnace was connected through the programmer to the recorder. The sample atmosphere was introduced into the furnace through the handle of the sample holder and dispersed at four points just above the top of the crucibles. The atmosphere filled the furnace and then vented at the furnace top. All data were collected using chromel–alumel thermocouples for the differential temperature and a Platinel I thermocouple to measure the furnace temperature with alumina as reference material.

The graphite crucibles were manufactured to NUMEC design by POCO Graphite, Inc. from Spectro AZ grade graphite, which has high purity, strength, and electrical resistivity and low-thermal conductivity. These graphite crucibles were required due to reaction of the tetrafluoroborates with the standard quartz crucibles supplied with the Fisher system. A drawing of the graphite crucible is shown in Fig. 1.

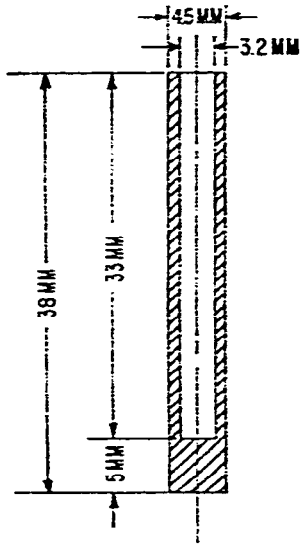


Fig. 1. Graphite crucible (all dimensions ± 0.1 mm, except O. D. which is $^{+0.0}_{-0.1}$ mm).

Material used for this investigation was purchased from ALFA Inorganics and was 99%+ pure, the only exception being the cesium tetrafluoroborate which was prepared at our laboratory. The compounds were used as received except for the lithium tetrafluoroborate which was ground to size just before use.

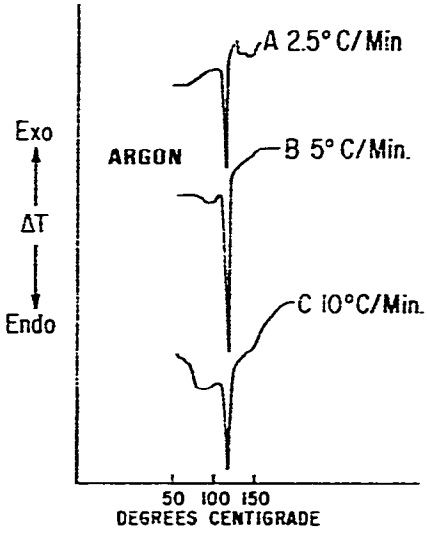
The first compound investigated was lithium tetrafluoroborate. Table I is a summary of the DTA analysis performed on this material. Curves A, B, and C were

TABLE I

DIFFERENTIAL THERMAL ANALYSIS OF LITHIUM TETRAFLUOROBORATE

Curve	*Atmosphere*	*Weight (mg)*	*Heating rate (°C/min)*	*Transition temp. (°C)*
A	Argon 2 SCF/H	170	2.5	111
B	Argon 2 SCF/H	160	5.0	115
C	Argon 2 SCF/H	160	10.0	115
D	Air, Static	200	2.5	109
E	Air, Static	200	5.0	110
F	Air, Static	200	10.0	108

obtained with a flowing argon atmosphere of 2 SCF/H while D, E, and F were run in a static ambient environment. The transition which appears at 111–115 °C for the flowing argon and at 108–110 °C for the static environment is the rhombic-to-cubic transition. Peak height increases with increased heating rate while the temperature of the transition remains fairly constant. There is an observed change in the transition temperature which is attributed to the atmosphere in the furnace. Figs. 2 and 3 are the curves for lithium tetrafluoroborate.



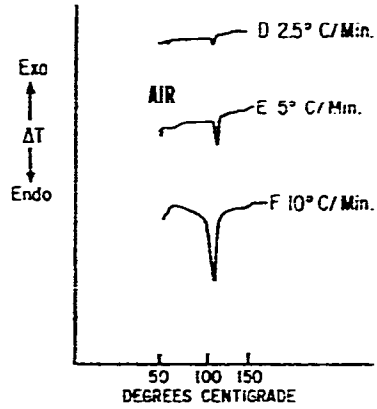


Fig. 2. DTA curves of lithium tetrafluoroborate (curves A, B, and C).

Fig. 3. DTA curves of lithium tetrafluoroborate (curves D, E, and F).

The next in the series is sodium tetrafluoroborate. Table II is a summary of this analysis. Curves G, H, and I where obtained with a flowing argon atmosphere of 2 SCF/H while J, K, and L were run in a static ambient environment. The rhombic-to-cubic transition appears at a temperature of 246–247 °C for the flowing argon system and at 238–240 °C for the static system. Again, peak height increases with increased heating rate while the transition temperature remains constant. Also, a lowering of the transition temperature when going from the argon system to a static system is observed. Figs. 4 and 5 are the curves for sodium tetrafluoroborate.

TABLE II

DIFFERENTIAL THERMAL ANALYSIS OF SODIUM TETRAFLUOROBORATE

Curve	*Atmosphere*	*Weight (mg)*	*Heating rate (°C/min)*	*Transition temp. (°C)*
G	Argon 2 SCF/H	270	2.5	247
H	Argon 2 SCF/H	270	5.0	246
I	Argon 2 SCF/H	270	10.0	247
J	Air, static	200	2.5	238
K	Air, static	200	5.0	240
L	Air, static	200	10.0	240

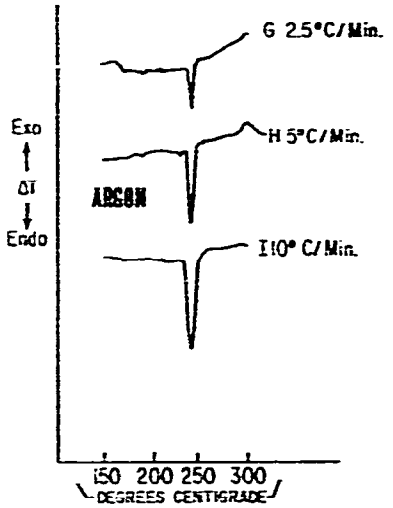


Fig. 4. DTA curves of sodium tetrafluoroborate (curves G, H, and I).

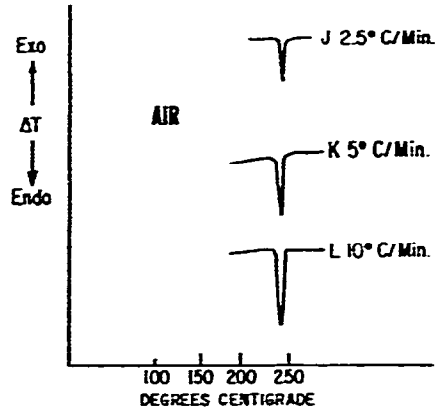


Fig. 5. DTA curves of sodium tetrafluoroborate (curves J, K, and L).

Potassium tetrafluoroborate is the next compound of interest. Table III is a summary of the DTA analysis performed. Curves M, N, and O were obtained with a flowing argon atmosphere of 2 SCF/H while P, Q, and R were run in a static ambient environment. With this compound the rhombic-to-cubic transition is shown to take place at a temperature of 278–279 °C for the flowing argon system and 278–280 °C for

TABLE III

DIFFERENTIAL THERMAL ANALYSIS OF POTASSIUM TETRAFLUOROBORATE

Curve	*Atmosphere*	*Weight (mg)*	*Heating rate (°C/min)*	*Transition temp. (°C)*
M	Argon 2 SCF/H	200	2.5	278
N	Argon 2 SCF/H	200	5.0	278
O	Argon 2 SCF/H	200	10.0	279
P	Air, static	200	2.5	280
Q	Air, static	200	5.0	280
R	Air, static	200	10.0	278

the static system. Again as in previous runs, peak height increases with heating rate. The transition temperature remains fairly constant both with heating rate and furnace atmosphere for this compound. Figs. 6 and 7 are of the potassium tetrafluoroborate.

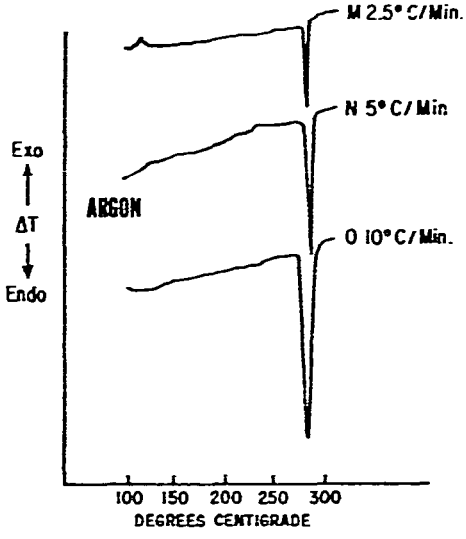


Fig. 6. DTA curves of potassium tetrafluoroborate (curves M, N, and O).

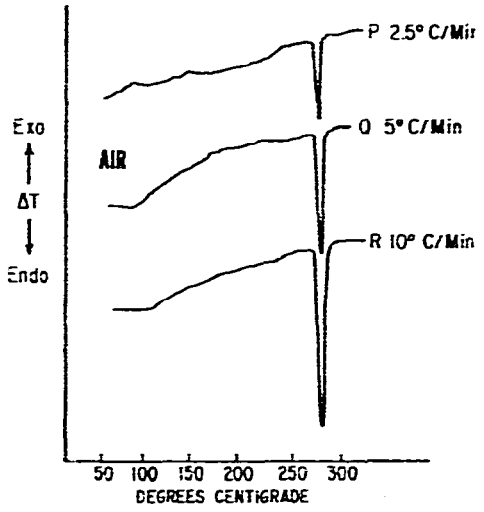


Fig. 7. DTA curves of potassium tetrafluoroborate (curves P, Q, and R).

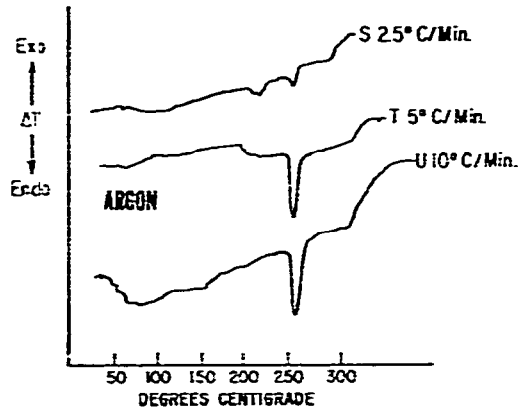
The fourth compound in this series is rubidium tetrafluoroborate. Table IV is a summary of the DTA data for this material. Curves S, T, and U were obtained in a flowing argon atmosphere of 2 SCF/H while V, W, and X were run in a static ambient environment. The rhombic-to-cubic transition for rubidium tetrafluoroborate is shown to take place at 250–251 °C for the argon system and 245–247 °C for the static

TABLE IV

DIFFERENTIAL THERMAL ANALYSIS OF RUBIDIUM TETRAFLUOROBORATE

Curve	*Atmosphere*	*Weight (mg)*	*Heating rate (°C/min)*	*Transition temp. (°C)*
S	Argon 2 SCF/H	180	2.5	251
T	Argon 2 SCF/H	180	5.0	251
U	Argon 2 SCF/H	180	10.0	250
V	Air, static	200	2.5	245
W	Air, static	200	5.0	247
X	Air, static	200	10.0	247

system. Again as for the three previous compounds, the height increases with heating rate while the transition temperature remains fairly constant with heating rate. Also as in lithium and sodium tetrafluoroborate the furnace atmosphere has the effect of lowering the transition temperature in the static system. Figs. 8 and 9 are the curves for rubidium tetrafluoroborate.



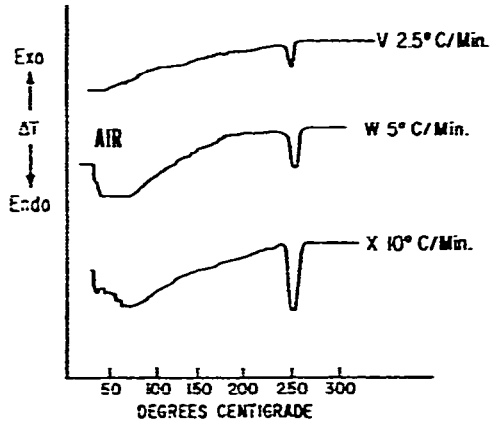


Fig. 8. DTA curves of rubidium tetrafluoroborate (curves S, T, and U).

Fig. 9. DTA curves of rubidium tetrafluoroborate (curves V, W, and X).

The final compound in the series is cesium tetrafluoroborate. Table V is a summary of the data collected for this compound. Curves Y, X, and AA were obtained in a flowing argon atmosphere of 2 SCF/H while BB, CC, and DD were run in a static ambient system. The temperature of the rhombic-to-cubic transition for this compound is 169–170 °C for the argon system and 164–169 °C for the static

TABLE V

DIFFERENTIAL THERMAL ANALYSIS OF CESIUM TETRAFLUOROBORATE

Curve	*Atmosphere*	*Weight (mg)*	*Heating rate (°C/min)*	*Transition temp.-(°C)*
Y	Argon 2SCF/H	250	2.5	170
Z	Argon 2SCF/H	250	5.0	169
AA	Argon 2SCF/H	250	10.0	170
BB	Air, static	200	2.5	166
CC	Air, static	200	5.0	164
DD	Air, static	200	10.0	169

system. As noted in all the previous compounds studied in this series, the peak height increases with the heating rate while the temperature of the transition remains constant. It is also noted that there is an atmosphere effect on the transition temperature of this compound as on four of the five reported here. This effect is one of lowering the temperature when going from a flowing argon atmosphere to static ambient conditions. Figs. 10 and 11 are the curves for cesium tetrafluoroborate.

The transition temperatures for sodium and potassium tetrafluoroborate have been reported in the literature. The transition temperatures for lithium, rubidium, and cesium tetrafluoroborates have not been. The reported transition temperature for sodium tetrafluoroborate of 298 °C appears to be either in error by some 50–60 degrees or has been mis-translated from the German to the English reference.

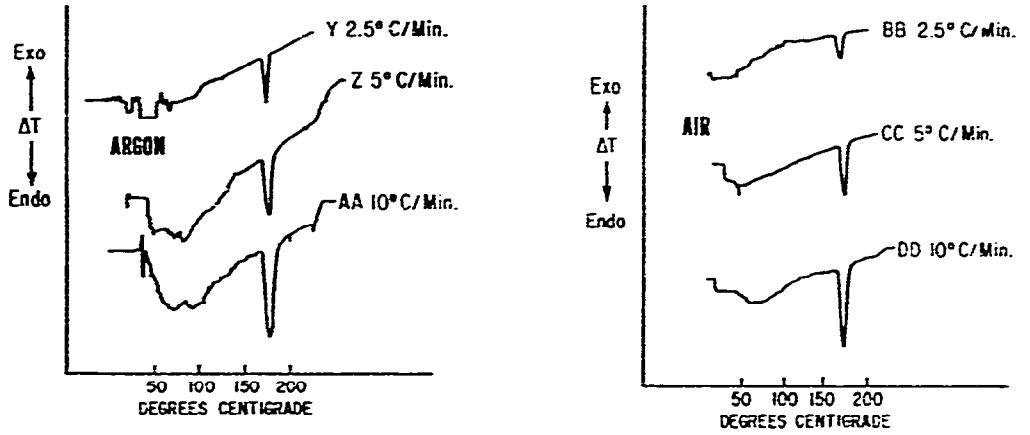


Fig. 10. DTA curves of cesium tetrafluoroborate (curves Y, Z, and AA).

Fig. 11. DTA curves of cesium tetrafluoroborate (curves BB, CC, and DD).

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