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CALORIMETRIC HEAT OF TRANSITION ASSIGNMENTS BY MICROCOMPUTER-BASED DIFFERENTIAL THERMAL ANALYSIS. PART I. THE α–δ (MONOCLINIC TO CUBIC) TRANSITION OF BISMUTH(III) OXIDE

C.M. EARNEST

Department of Chemistry, Berry College, Mount Berry Station, Rome, GA 30149 (U.S.A.)

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ABSTRACT

The enthalpy change (ΔH) associated with the α–δ (monoclinic to face-centered cubic) crystalline transition for a high purity specimen of bismuth(III) oxide was experimentally measured. The mean value obtained by numerous operators of the same model of a commercially available computerized differential thermal analysis (DTA) system is reported. These data were collected at three different heating rates and for a wide variety of sample sizes. The mean value obtained in this study (71.2 J g^{-1}) was compared with previously published results of other workers for the same crystalline transition. The precision of the measurements reported here was statistically determined.

INTRODUCTION

This thermal analysis study of bismuth(III) oxide was conducted for both its academic interest and its industrial importance. In the author's present position there existed a need for a training exercise for students to utilize the "DSC Mode" of a commercial DTA instrument. The other major reason for conducting this study was due to the inconsistency and wide range of the heat of transition values which have been published for the α–δ transition in bismuth(III) oxide Bi_2O_3.

Bismuth(III) oxide is the only oxide of bismuth which has been definitely isolated in a pure state [1]. Thus, in most cases, it will simply be referred to as bismuth oxide for the remainder of this paper. Bismuth oxide, Bi_2O_3, has been found to be a satisfactory constituent of optical glasses. It is also used as an ingredient in fluxes for fired on types of conductive silver paints. Calcined bismuth oxide can be used singly as a flux to bond metallic silver flake to ceramic bodies. Bismuth oxide is also used as a component in a number of catalysts.

Elemental bismuth belongs to the periodic group VA and has a valence shell electronic configuration of $6S^2 6P_x^1 6P_y^1 6P_z^1$. Bismuth is the most metallic member of periodic group VA and exhibits a +3 oxidation state in the vast majority of its ionic compounds. This is readily understood in terms of the loss of the three 6P electrons leaving the filled 6S orbital as a lone pair of electrons.

Bismuth oxide, Bi_2O_3, has a complicated polymorphism. This polymorphic behavior was investigated by workers as long ago as 1903 [2]. Four polymorphs of Bi_2O_3 are reported in the literature. The stable low temperature form is the monoclinic (α) phase which on heating transforms to the high temperature cubic (δ) phase at 730 °C. This phase is then stable up to the melting point near 810 °C. The fusion (δ–liquid) endotherm for bismuth oxide is difficult to quantify thermodynamically owing to the reactivity of the liquid phase with many of the commonly used differential thermal analysis (DTA) and differential scanning calorimetry (DSC) sample pans or liners. The solid–solid (α–δ) transition is easily studied, however, by the technique of DTA. The technique of thermomechanical analysis (TMA) may also be employed to study the solid–solid (α–δ) transition as well as the fusion transition of the cubic (δ) phase.

On cooling Bi_2O_3 from the melt, other transitions may be observed. These were reviewed and described by Harwig and Gerards [3] along with a complete study of Bi_2O_3 polymorphic behavior. Hysteresis phenomena are observed on cooling the high temperature (δ) phase. Two metastable phases at room temperature have been observed in quenching and decomposition experiments. These are a tetragonal (β) phase and a body-centered cubic (γ) phase [4]. Table 1 describes the phase transitions observed on heating and cooling when performing DTA or DSC. The temperatures given for the transitions observed on cooling were taken from the work of Harwig and Gerards [3].

In the study which follows, these transitions will be observed by the computerized technique of differential thermal analysis. Particular interest

TABLE 1

Phase transitions observed on heating and cooling bismuth(III) oxide (from Harwig and Gerards [3])

Heating

$\text{Monoclinic } (\alpha) \xrightarrow{730\,^\circ\text{C}} \text{face-centered cubic } (\delta) \xrightarrow{825\,^\circ\text{C}} \text{liquid}$

Transitions on cooling from melt

$\text{liquid} \xrightarrow{<825\,^\circ\text{C}} \text{face-centered cubic } (\delta) \xrightarrow{650\,^\circ\text{C}} \text{tetragonal } (\beta) \xrightarrow{330\,^\circ\text{C}} \text{monoclinic } (\alpha)$

or

$\text{liquid} \xrightarrow{<825\,^\circ\text{C}} \text{face-centered cubic } (\delta) \xrightarrow{639\,^\circ\text{C}} \text{body-centered cubic}^{a} \ (\gamma)$

$\text{followed by body-centered cubic}^{a} \ (\gamma) \xrightarrow{500\,^\circ\text{C}} \text{monoclinic } (\alpha)$

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[a] The γ phase may persist to room temperature.

will be given to the assignment of the endothermic heat associated with the α–δ (monoclinic to face-centered cubic) crystal phase transition observed on heating a high purity bismuth oxide specimen. The average result obtained for the heat of transition by numerous operators of the same model of computerized differential thermal analyzer (Perkin–Elmer DTA 1700) will be compared with published values found in the existing scientific literature. In order to give some insight into the calorimetric accuracy of this work, the heat of transition for the orthorhombic (γ) to hexagonal (β) phase in barium carbonate was also assigned. This study is presented as a separate paper [5].

EXPERIMENTAL

All DTA thermal curves were obtained using a Perkin–Elmer DTA 1700 high temperature differential thermal analysis system. A Perkin–Elmer model 3700 computer used in conjunction with a Perkin–Elmer 2 graphics plotter, and DTA standard software package was employed as the data-handling device. When used with thermal analysis systems, this data handling device is referred to by the vendor as the Thermal Analysis Data Station (TADS). For all studies, the DTA 1700 was used in the DSC mode of operation. The DTA instrument was temperature calibrated using high purity (99.999%) aluminum shot (lot # 070880) which was obtained from Alfa Products, Thiokol/Ventron division (Danvers, MA, U.S.A.).

The DSC ordinate heat flow axis of the DTA 1700 was also calibrated using the same aluminum standard from Alfa Products. This calibration is achieved by entering a factor into the thermal analysis software (DTA standard). This factor is determined experimentally by ratioing the known heat of fusion of aluminum to that which is experimentally observed using the DTA 1700. In the work which follows, an average value of 1.27 was used for the DSC ordinate calibration factor.

A high purity (Puratronics 99.999%, Batch S87443/A) bismuth oxide specimen was purchased from Alfa Products (Danvers, MA).

All DSC thermal curves of this work were obtained using 60 mm^3 ceramic liners in the DTA sample holder cups. Flowing nitrogen was used as the dynamic purge atmosphere in the analyzer cell. Heating rates of 10, 20, and 30 °C min^{-1} were used in the quantitative heat of transition assignments of this study. Fresh, unused liners were employed for the sample cup for each heating run in the DTA. After each sample specimen was placed into the ceramic liner, calcined alumina was placed over the sample material. The reference cup of the DTA cell was filled with calcined alumina powder and was used in all studies as the reference material. All samples for analysis were weighed (by difference) using either a Perkin–Elmer AD-2Z or an AD-6 autobalance.

RESULTS AND DISCUSSION

It was stated earlier in this work that these thermodynamic data were generated as a part of training exercises for students at Berry College as well as for participants in customer-training courses which were taught by the author for the instrument manufacturer. The instrument used in these exercises has two modes of operation. This dual mode of operation is made possible by microcomputer firmware components which are incorporated into the instrument hardware. The diagram shown in Fig. 1 describes how the differential output from two Pt–Pt(10% Rh) thermocouples may undergo microcomputer signal conditioning by either one of two different modes which is selected by the operator prior to performing the thermal analysis.

In all of the DTA work which is presented here, Mode 2 of operation of the instrument (as shown in Fig. 1) was employed. In this case the microcomputer signal conditioning serves to adjust the DTA peak area in a manner which enables the instrument to be used for heat of transition assignment. This ordinate signal factoring versus temperature has been previously described [4,6] by the author and will not be further discussed here. It is recommended by the manufacturer that any quantitative energy assignments which are to be made with the instrument employed in this work should be performed using Mode 2 ("DSC Mode") of operation.

Figure 2 shows how the sample is actually positioned in the DTA cell. The two Pt–Pt(10% Rh) thermocouples are physically supported in ceramic support tubes which are positioned vertically by placing each into the V grooves of a ceramic support base. This positioning is shown in Fig. 2. Purge gas enters the DTA cell through a ceramic tube (1/16 inch I.D.) which is positioned by a third V groove located on the back side of the support base. Thus, the purge gas is preheated prior to actually entering the measuring cell.

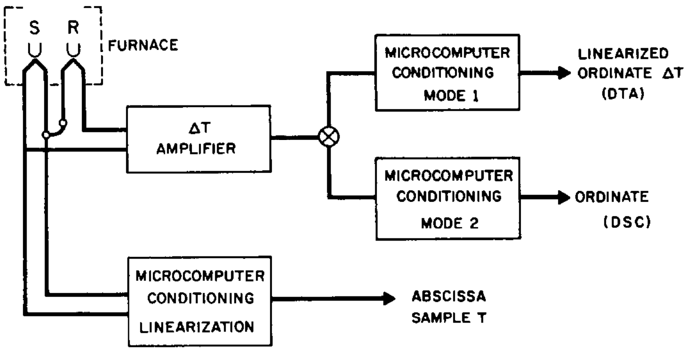

Fig. 1. Block diagram describing microcomputer signal conditioning capabilities of the DTA employed in this study.

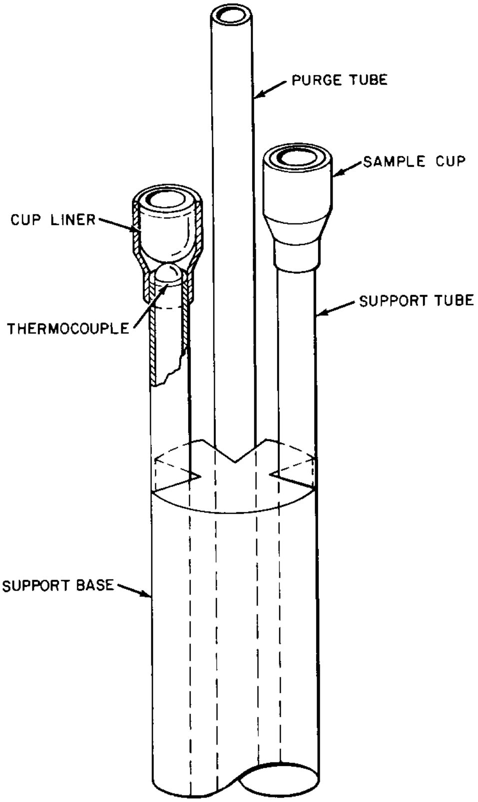

Fig. 2. Descriptive drawing of the physical arrangement of the DTA analyzer cell components.

A platinum sample cup is mounted over each of the two Pt–Pt(10% Rh) thermocouples. A small amount of calcined alumina is then placed around the thermocouples in each sample cup. In this work, the analyte sample material was placed into a 60 mm ceramic liner which was then positioned into the left thermocouple sample cup. Similarly, a 60 mm ceramic liner filled with calcined alumina was placed in the reference (right) sample cup. The entire sample cell assembly (shown in Fig. 2) was then enclosed by installing an alumina-based ceramic furnace tube. Using this arrangement, the purge gas effluent exits from an orifice at the bottom of the DTA cell assembly.

Figure 3 describes the appearance of all DTA thermal curves for the Bi_2O_3 specimens on initial heating with the DTA 1700 instrument. This hard copy printout (Fig. 3) represents the data as taken on the TADS CRT screen in the SET UP program of this software package. In this graphical presentation, the ordinate signal is displayed versus the actual sample temperature as measured by the left-hand thermocouple in the cell. Figure 3 also shows the assignment of the two endothermic peak minima by an optional peak search

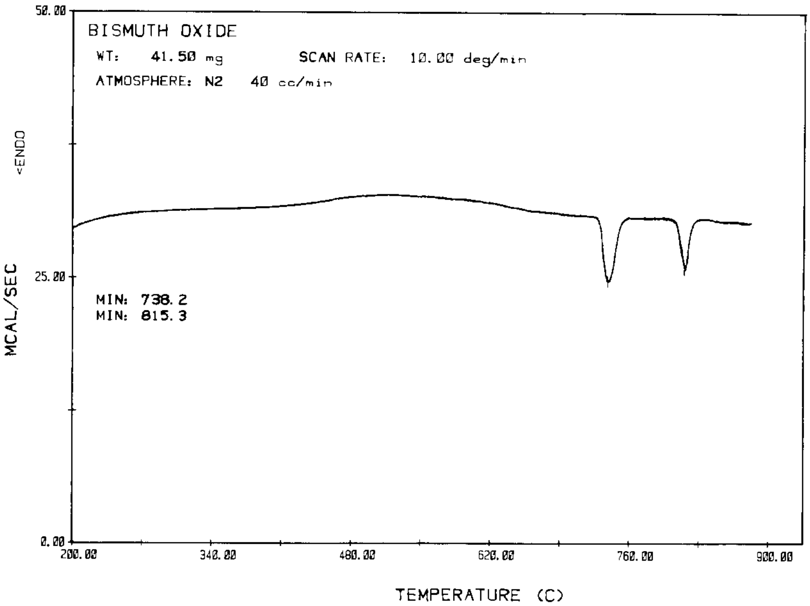

Fig. 3. DTA thermal curve as originally displayed in SET UP program by TADS CRT screen. Peak search results are also shown.

routine which is executed immediately after the last data point is received by the TADS computer. The lower temperature endotherm with a peak minimum at 738.2° C corresponds to the α–δ crystalline transition and the higher temperature endotherm, having a peak maximum at 815.3° C, is the melting endotherm for the high temperature phase. The data in the form displayed by Fig. 3 must be redistributed on a time base (abscissa) in order to perform quantitative peak area calculations. This is achieved by a "GO TO ANALYSIS" command in the DTA standard software. After the data are spread on a time base, the abscissa of the thermal curve is labeled with actual sample temperature information. Thus, these actual sample temperature values correspond to the sample temperature at various times in the analysis.

Figure 4 shows a DTA thermal curve after executing the "GO TO ANALYSIS" command. Once the data has reached the analysis program, many data manipulation algorithms may then be executed. The thermal curve shown in Fig. 4 has been rescaled by a "RESCALE T" command so that only the data points between 500 and 910° C are displayed.

This heating run (Fig. 4) of the high purity Bi_2O_3 specimen was obtained for a 35.74 mg sample using a heating rate of 10° C min^{-1}. Flowing nitrogen of 40 cc min^{-1} was used as the purge gas. This DSC thermal curve is just one of 15 such analyses which were conducted for this Bi_2O_3 specimen. These analyses were performed by either Berry College students on the DTA instrument located on campus here or by participants of the customer-train-

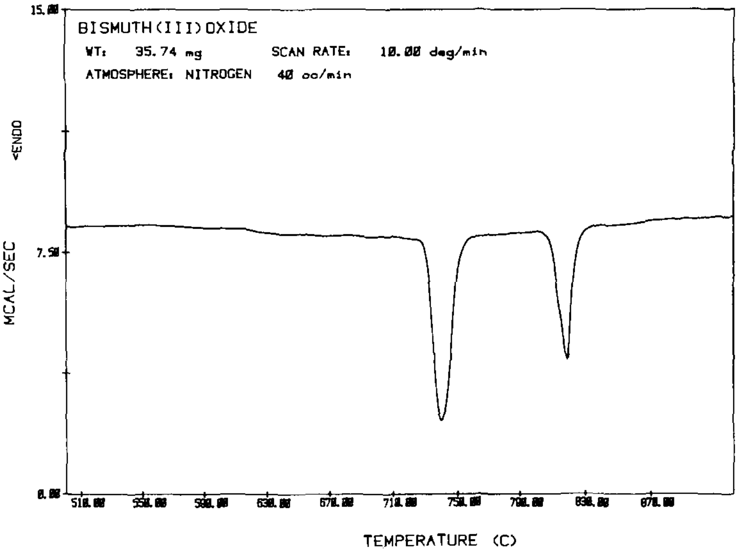

Fig. 4. Rescaled DTA thermal curve for Bi_2O_3 after redistribution of data points in analysis program.

ing courses for this instrument held in Norwalk, CT. Six different instruments were employed and 12 different operators participated in these quantitative exercises. The remaining three analyses were made by the author.

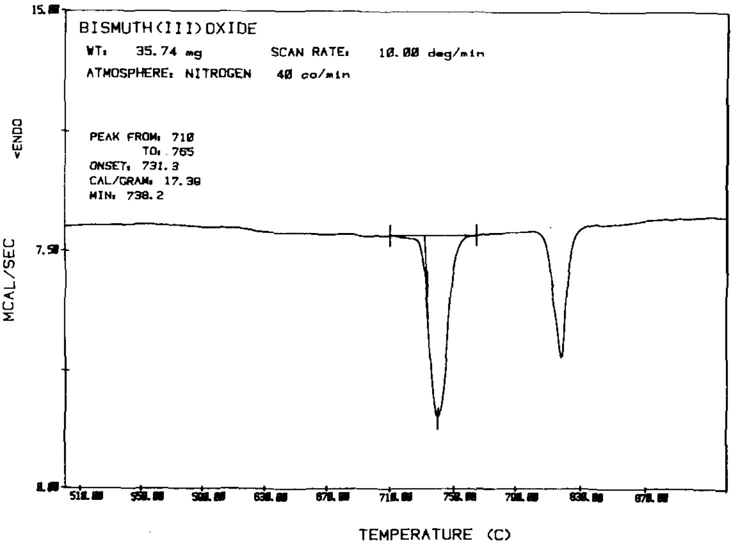

Fig. 5. Rescaled DTA thermal curve for Bi_2O_3 showing heat of transition assignment with peak analysis routine of DTA software.

In all cases, the heat of transition for the crystalline transition was assigned using the DTA standard software "Peak Analysis" algorithm. Figure 5 shows the same DSC thermal curve as given in Fig. 4 with peak analysis. One can see that for this experimental run an endothermic heat of transition of 17.4 cal g^{-1} (72.7 J g^{-1}) was measured for the α–δ transition. This thermal curve reflects the use of English units with the software package. The operator may choose either English or metric units when setting up the analysis in the SET UP program. Although metric units are the preferred, the choice was left to the student operator. Some chose metric units and others chose English units.

RESULTS

Table 2 gives the values in Joules per gram obtained from 13 of the 15 DSC runs obtained in this work. Two of the 15 determinations were statistically rejected using the $\pm 3\sigma$ criterion. These values represent rising temperature experiments performed at 10, 20, and 30 °C $\min^{-1}$. A wide variety of sample sizes were used in these experiments ranging from as small as 31.6 mg to 85.2 mg of sample. From these results one can see that the normalized peak area (J g^{-1}) did not vary with sample size or heating rate. It should be pointed out that the use of heating rates greater than 30 °C $\min^{-1}$ leads to incomplete separation of the two endothermic transitions when using sample sizes of the magnitude of those employed in this study.

TABLE 2

Results of this study for the heat of transition ($\alpha-\delta$) of bismuth(III) oxide

Heating rate (°C $\min^{-1}$)	Sample weight (mg)	$\Delta H(\alpha-\delta)$ [a] (J g^{-1})
10	46.5	71.6
10	43.4	74.9
10	85.2	71.6
10	67.7	68.6
20	37.9	68.2
20	71.3	76.6
20	69.6	71.6
20	35.7	72.0
20	31.6	70.7
20	51.2	71.1
30	52.2	69.9
30	73.4	71.1
30	53.6	68.3

[a] Average $\bar{x} = 71.2$ J g^{-1}; $\bar{d} = \pm 1.52$; $\sigma = 2.25$; range = 8.4 J g^{-1}.

As can be observed in Table 2, the data set gave a mean value of 71.2 J g^{-1} and a median value of 71.1 J g^{-1}. The dispersion of the values of the set is described by a range of 8.4 J g^{-1}, an average deviation of ±1.52 J g^{-1}, a standard deviation δ of 2.25 J g^{-1}, and a relative standard deviation (rsd) of 3.16%. It should be pointed out that the precision of such quantitative assignments using DSC is highly dependent upon the accuracy and precision of the sample-weighing step which precedes the actual thermal analysis. This is particularly true for data obtained in training exercises such as these.

COMPARISON OF DATA WITH PREVIOUS STUDIES

The rather wide range of measured values for the heat of transition was one of the primary reasons for conducting this study of bismuth oxide. Table 3 gives a listing of published results which arise from experimentally measured heats of transition. The range of these values (22.5 J g^{-1}) is quite large and span a time period of 15 years. Three of the reported values [7–9] were obtained using DTA while the other [10] was obtained using a power-compensated DSC. This set of values gives a mean published value of 75.7 J g^{-1}. These measured values, although quite dispersed, are an improvement over the non-measured (calculated) values which for the most part preceded them in the scientific literature.

The mean value for the measured heat for the transition reported in the literature (75.7 J g^{-1}) is 4.5 J g^{-1} higher than that obtained experimentally in this work (71.2 J g^{-1}). Of the previously published heat of transition values, that of Gattow and Schultze [9] (75.3 J g^{-1}) is in closest agreement with the mean experimental value obtained in this work. The Gattow and Schultze value is also in good accord with the mean literature value given in Table 3.

TABLE 3

Published experimental results for $\Delta H(\alpha-\delta)$ from previous studies on the $\alpha-\delta$ transition in bismuth(III) oxide

	kcal mol^{-1}	cal g^{-1}	J g^{-1}
Rao et al. [8]	8.8	18.9	79.1
Levin and McDaniel [9]	9.5	20.4	85.4
Gattow and Schultze [10]	8.4	18.0	75.3
Harwig and Gerards [3]	7.1	15.2	62.9
Average	8.4	18.1	75.7
Range	2.4	5.2	22.5
Average deviation $\bar{d}$	±0.7	±1.8	±6.6

CONCLUSION

With this wide range of values, one can only speculate as to which is the most accurate. Obviously, the author favors the value (71.2 J g^{-1}) which was experimentally determined in this work using a modern microprocessor-based instrument and computerized data-handling algorithms. One item which does stand out in one of the previously published results is that Rao et al. [8] employed quartz and potassium sulfate as enthalpy standards upon which their experimental value of 79.1 J g^{-1} is based. It is well known that quartz cannot be used as an enthalpy standard owing to variations in crystallinity. Furthermore, modern published values for the crystalline transition of potassium sulfate range from as low as 7.73 cal g^{-1} (32.3 J g^{-1}) [11] to as high as 12.05 cal g^{-1} (50.4 J g^{-1}) [12]. The NBS Circular [13] gives a value of 11.13 cal g^{-1} (46.5 J g^{-1}). Thus, potassium sulfate should not be used as an enthalpy standard owing to this disagreement.

The value published by Harwig and Gerards [3] for the transition may also be affected similarly by the choice of potassium chromate, K_2CrO_4, as the energy standard. There is also considerable disagreement concerning the endothermic heat associated with this transition at 667 ° C. Some commonly used published heat of transition values for potassium chromate are 12.61 cal g^{-1} (52.7 J g^{-1}) [13], 9.26 cal g^{-1} (38.7 J g^{-1}) [12], and 8.52 cal g^{-1} (61.2 J g^{-1}) [11]. Thus, potassium chromate is a questionable enthalpy standard for heat of transition measurements.

Since the bismuth oxide studies of this work were performed in alumina-based ceramic liners, no report is given here for the heat of transition associated with the liquid fusion endotherm. The chemical corrosion of alumina by molten bismuth oxide was adequately pointed out by Harwig and Gerards [3].

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