Thermochimica Acta, 28 (1979) 121–131

THE POLYMORPHISM OF BISMUTH SESQUIOXIDE

H. A. HARWIG AND A. G. GERARDS
Inorganic Chemistry Department, State University Utrecht, Croesestraat 77A, Utrecht (The Netherlands)

(Received 23 January 1978)

ABSTRACT

The polymorphism of Bi_2O_3 has been studied by means of differential thermal analysis and electrical conductivity measurements, thermogravimetry, high temperature X-ray powder diffraction, and differential scanning calorimetry. Two stable and two metastable phases have been observed. Transition temperatures and enthalpies are reported.

INTRODUCTION

The polymorphism of Bi_2O_3 has been the subject of several investigations[1–12]. Levin and Roth[7] have reviewed the work prior to 1964. Four polymorphs of Bi_2O_3 have been reported in the literature. The phase transition of the low temperature monoclinic α-phase to the high temperature cubic δ-phase at approximately 730°C has been observed by several investigators[6–9]. The δ-phase is stable up to the melting point at 825(5)°C[7, 12]. The data regarding the enthalpy of the $\alpha \rightarrow \delta$ transition and the enthalpy of fusion, however, are inconsistent[6, 8, 9, 13, 14]. The extremely large transition enthalpy $\Delta H(\alpha \rightarrow \delta) = 28$ kcal/mole given by Gattow and Schröder[6] and cited in many thermodynamic tables is incorrect, since it is based on contradictory observations[2, 6, 14].

On cooling from the high temperature phase, hysteresis phenomena and the occurrence of intermediate metastable phases near 650°C have been reported[8–11, 15]. Two metastable phases at room temperature have been observed in quenching and decomposition experiments, i.e. the tetragonal β phase[3, 4, 8] and the bcc γ-phase[4, 7]. The available data on the behaviour of Bi_2O_3 on cooling are inconsistent and incomplete. In Table 1, temperatures and enthalpies of the transitions in Bi_2O_3 are summarized together with the results of the present investigation. Recent papers by Takahashi and coworkers on the electrical properties of mixed oxides in the systems Bi_2O_3–Me_xO_y (e.g. Me = Sr, Ca, La, W)[16, 17] have provoked a renewed interest in the polymorphism of Bi_2O_3. Takahashi et al.[16] recognized that the high temperature phase of Bi_2O_3 shows high ionic conductivity and can be used as a solid electrolyte. The electrical properties[18] and a more detailed description of the structures[19] of the

TABLE 1

TEMPERATURES T(°C) AND ENTHALPIES ΔH (KCAL MOLE^{-1}) OF TRANSITIONS IN Bi_2O_3

		This work		*Rao*[9]	*Levin*[12]	*Gattow*[8]	*Gattow*[6]	*Levin*[13]
		DTA	*DSC*	*DTA*	*DTA*	*DTA*	*DTA*	
$\alpha \rightarrow \delta$	T	729(2)	730(1)	727	730	710–740	717(7)	
	ΔH		7.06(6)	8.8(4)	9.5(3)[b] 10.2(2)[c]	8.4(3)[d]	28(1)[e]	
$\delta \rightarrow$ L	T	824(2)			825	824(2)	824(2)	825(3)
	ΔH	2.6(2)			3.84(8)[b] 3.86(6)[c]			2.05(5)[f]
$\delta \rightarrow \beta$	T	650(2)	649(2)	630[a]		660–640		
	ΔH		5.19(6)	6.7		2.0(5)[d]		
$\beta \rightarrow \delta$	T	662(2)	667(1)					
	ΔH		5.19(6)					
$\beta \rightarrow \alpha$	T	652–534	576–497	543[a]		640–430		
	ΔH		1.74(5)	2.1		6.4(8)[d]		
$\delta \rightarrow \gamma$	T	639(2)	643(2)					
	ΔH		5.05(5)					
$\gamma \rightarrow \delta$	T	663(2)	652(2)					
	ΔH		5.05(5)					
$\gamma \rightarrow \alpha$	T	639–543	604–562					
	ΔH		1.86(5)					

[a] The intermediate phase was assumed to be the β-phase by Rao et al.

[b] Internal standard K_2SO_4.

[c] Internal standard Ag.

[d] Calculated with $\Delta H(\delta \rightarrow \mathrm{L}) = 2.05$ (ref. 13). From Fig. 7 (ref. 8) $\Delta H(\delta \rightarrow \beta) \cong 3\ \Delta H(\beta \rightarrow \alpha)$, which suggests the interchange of the data for the $\delta \rightarrow \beta$ and $\beta \rightarrow \alpha$ transitions.

[e] Calculated with $\Delta H(\delta \rightarrow \mathrm{L}) = 6.8$ (refs. 2, 14).

[f] Calculated by application of the Clausius–Clapeyron equation on the liquidus data of the Bi_2O_3–B_2O_3 system.

various phases of Bi_2O_3 will be published elsewhere. In the present study, differential thermal analysis and electrical conductivity measurements, thermogravimetry, and high temperature X-ray powder diffraction were used to detect the phase transitions in Bi_2O_3 and to establish the presence and the regions of existence of the metastable phases. The enthalpies of transition were determined by means of differential scanning calorimetry.

EXPERIMENTAL

Reagents

As sample material, Bi_2O_3 (Kawecki-Billiton, 99.99% pure) was used. Emission spectroscopical analysis showed Si (0.001 wt.%) as the main impurity. Except for Fe (0.0002 wt.%) and Mg (0.00005 wt.%), no metals could be detected. Bi_2O_3 (Baker AR, 99.9% pure) was used in some experiments. The main impurities detected in this material were Na (0.03 wt.%) and Si (0.02 wt.%).

Differential thermal analysis and electrical conductivity measurements

The corrosive nature of molten and high temperature phase Bi_2O_3 makes special demands on the apparatus used. An apparatus that was originally described by Bottelberghs and van Buren[20] for DTA experiments proved convenient. Sample holders of Pt, Au, Al_2O_3 (Degussa Al23) and ZrO_2 (Degussa Zr23) were used. Sample weights between 0.5 and 1.0 g were used to limit the contamination of the sample by the holder material. Moreover, only on large samples can the high electrical conductivity at high temperatures be measured. Provisions were made to the sample holder to permit a Kelvin-type of measurement[21], which was necessary in view of the high electrical conductivity. The thermocouple in the sample and a Pt sample holder served as the electrodes. The conductivity was measured at 1592 Hz by means of an autobalance bridge (Wayne Kerr 641B, range 10^2 to 10^{-7} Ω^{-1}) equipped with an automatic ranging system. The temperature accuracy was $\pm$ 2°C. The apparatus was calibrated at the solid state transition and melting temperature of Li_2SO_4. For DTA measurements, heating and cooling rates of 10°C min^{-1} were used, whereas for simultaneous DTA/EC, measurements rates of 1 and 3°C min^{-1} were necessary.

DTA–TG

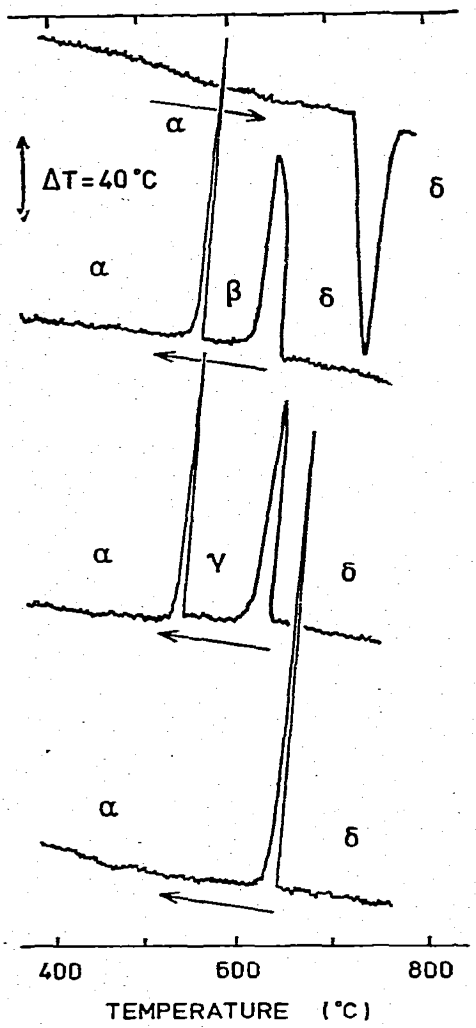
Thermogravimetry was performed with a Mettler TA2 and an atmosphere of purified argon or oxygen. The overall gas flow was 60 cm^3 min^{-1} and the heating rate 5°C min^{-1}. Platinum sample holders were used. The calibration of the temperature scale was checked with the solid state transition of K_2CrO_4 (NBS). The average sample weight was about 90 mg.

High temperature X-ray powder diffraction

A Guinier-Lenné camera (Enraf-Nonius) was used for the high temperature X-ray powder diffraction. Heating and cooling rates of 0.1 °C min^{-1} were employed. Due to the high absorption of Bi_2O_3, higher heating or cooling rates were not possible in dynamic measurements. A voltage stabiliser limited fluctuations in the oven power. At high temperatures, the Pt gauze of the sample holder served as a standard, since internal standards could not be used due to the corrosive nature of Bi_2O_3. At room temperature, Si (NBS, SRM 640) was used as reference material. The line positions were read from the exposures with a viewer (Enraf-Nonius). The cell dimensions were refined with a least squares program by Langford[22] using the Nelson–Riley extrapolation if the Si reference material could not be used.

DSC

The DSC measurements were performed with a Perkin-Elmer DSC-2 using Au sample holders. The apparatus was calibrated by means of the solid state transition of K_2CrO_4 (NBS). The peak areas were determined with a planimeter and a weighing procedure. The sample weight varied from 20 to 50 mg. Scanning speeds of 10 and 2.5°C min^{-1} were employed.



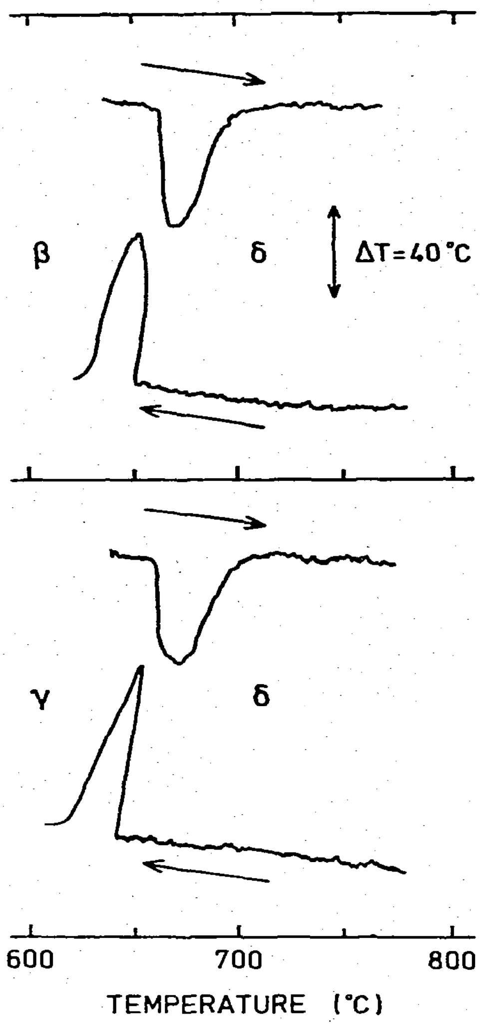


Fig. 1. DTA curves of Bi_2O_3. The measurements were taken below the melting point.

Fig. 2. DTA curves of $\delta \leftrightarrow \beta$ and $\delta \leftrightarrow \gamma$ transitions in Bi_2O_3.

RESULTS AND DISCUSSION

The colour of the samples changed from red-brown to black at the $\alpha \rightarrow \delta$ transition. Hysteresis effects in the colour change were visible on cooling.

Differential Thermal Analysis

The $\alpha \rightarrow \delta$ and $\delta \rightarrow$ L transitions were observed at 729(2) and 824(2) °C, respectively, in good agreement with the results of Levin and Roth[7]. On cooling, the δ-phase persisted 76–93 °C below 729 °C, if the temperature had been raised above 750 °C. Generally, this hysteresis preceded the formation of an intermediate phase. The transition of the intermediate phase to the low temperature phase was observed in the temperature range 650–497 °C in a series of measurements, and showed the typical behaviour of a transition from a metastable phase. In repeated cooling runs

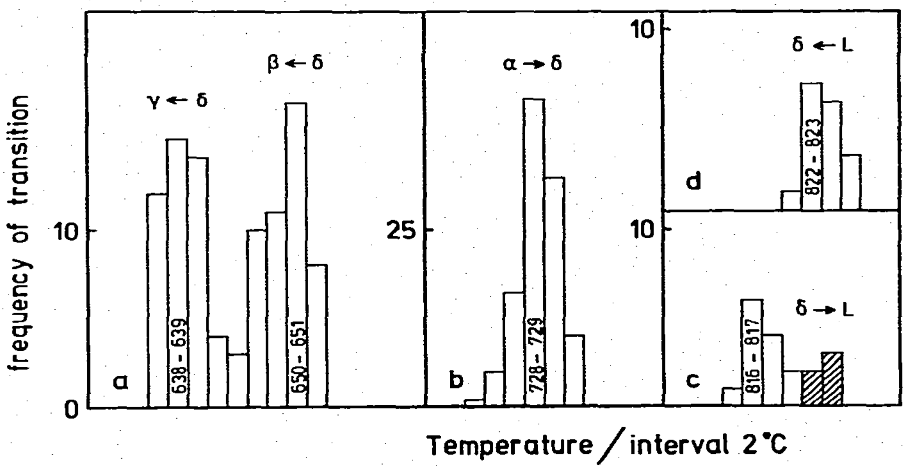


Fig. 3. Histograms of transition temperatures observed in Bi_2O_3. a, $\delta \rightarrow \beta$ 650(2) °C, $\delta \rightarrow \gamma$ 639(2) °C; b, $\alpha \rightarrow \delta$ 729(2) °C; c, $\delta \rightarrow$ L 824(2) °C from measurements 1–5 (shaded area); d, L $\rightarrow \delta$ 824(2) °C.

from the δ-phase, we noticed that the behaviour of the transition at approximately 645 °C was not fully reproducible. Apparently, two types of phase transitions occurred with a small temperature difference of about 10 °C. A series of heating and cooling runs was performed on each sample to check the significance of this phenomenon. Representative DTA curves are given in Figs. 1 and 2 for measurements performed below the melting point of Bi_2O_3. Identical results were obtained irrespective of the sample holder materials used. A histogram of the observed temperatures for 94 transitions from the δ-phase is given in Fig. 3a. For comparison, the histogram for 107 measurements of the $\alpha \rightarrow \delta$ transition temperature is given also (Fig. 3b). The observed peaks on cooling from the δ-phase clearly correspond to two different phase transitions, one at 650(2) °C and the other at 639(2) °C. The DTA peaks observed at these temperatures had a different shape (Figs. 1 and 2). A slight preference for the transition at 639 °C was observed for Bi_2O_3 supplied by Baker. Bi_2O_3 supplied by Kawecki showed a clear preference for the transition at 650 °C. Small hysteresis effects were noticed in the transitions from the metastable phases to the δ-phase (Fig. 2).

Representative DTA runs obtained with Pt sample holders in heating and cooling runs in which the melting point of Bi_2O_3 was exceeded are given in Fig. 4. The enthalpy of fusion is much smaller than the enthalpy of the $\alpha \rightarrow \delta$ transition. The ratio of the peak areas of the $\alpha \rightarrow \delta$ and the $\delta \rightarrow$ L transitions is 2.7(2). This value is in contrast to the value of 4.1(1) of Gattow and Schröder[6], but agrees well with the value of 2.5(1) of Levin and McDaniel[12]. Both intermediate phases were observed in different cooling runs. In some experiments, a small hump was observed in the DTA curve at approximately 730 °C. Interaction of the molten Bi_2O_3 with the Pt container had a distinct influence on the melting temperature. Histograms of 18 melting and 17 solidification temperatures are given in Fig. 3c and 3d, respectively. The melting temperature shifted gradually from 824 to 817 °C after the first measurements. With emission spectroscopical analysis, a concentration of 0.06 wt. % Pt was detected in the

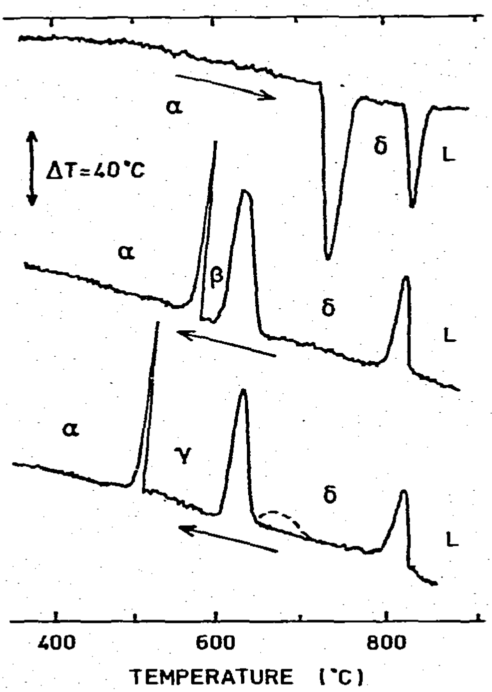


Fig. 4. DTA curves of Bi_2O_3 (Pt sample holder). Maximum temperature 890°C.

sample. Using Au and Pt sample holders, we found the same transition temperatures in Bi_2O_3. Several of the Pt and Au sample holders ruptured in the experiments due to the volume changes in Bi_2O_3 at the phase transitions.

Repeated heating and cooling runs in Al_2O_3 and ZrO_2 sample holders clearly indicated that chemical reactions occurred between molten Bi_2O_3 and the containers. The chemical corrosion of these very stable oxides emphasizes the corrosive nature of molten Bi_2O_3. The DTA results with Al_2O_3 sample holders, i.e. a gradual decrease of the heat effect of the $\alpha \rightarrow \delta$ transition and a gradually increasing new heat effect at 792°C which surpassed the melting peak, can be explained by the formation of the compound $BiAlO_3$ (ref. 23) or the compound $Bi_{15}AlO_{24}$ (ref. 24). The temperature of the $\alpha \rightarrow \delta$ transition was not affected. With emission spectroscopical analysis, 0.1 wt.% Al was detected in the sample. In DTA experiments with ZrO_2 containers, the $\delta \rightarrow$ L peak disappeared and the temperature of the $\alpha \rightarrow \delta$ transition decreased to approximately 700°C. A mixture of Bi_2O_3 and ZrO_2 (6: 1) heated at 860°C exhibited a high temperature phase which was metastable down to 591°C. The low temperature material was tetragonal with unit cell axes corresponding to those of β-Bi_2O_3. Solid solutions of Bi_2O_3 and ZrO_2 with a tetragonal structure have been reported earlier[25, 26]. These solid solutions may show fast ionic conduction at high temperature.

Differential thermal analysis and thermogravimetry

The DTA data obtained for the $\alpha \rightarrow \delta$ and $\delta \rightarrow$ L transitions with the Mettler TA2 agreed well with the data given in the previous section. In the DTA/TG measurement, only a small weight loss of 0.5 mg in the temperature range 100–320°C and of

0.4 mg in the temperature range 320–790 °C was observed, which can be attributed to the release of physisorbed water and of hydroxyl groups of the surface of the sample, respectively. The sample was kept at 790 °C under an argon flow. Under these circumstances, the weight loss in 53 h was lower than 0.02 mg, of the order of the long term instability of the apparatus. No weight change was detected when the atmosphere was changed by the introduction of oxygen. Hence we conclude that no appreciable deviations from stoichiometry occur in solid Bi_2O_3.

High temperature X-ray powder diffraction

The cell dimensions of the α-phase are in agreement with those obtained by Malmros[27]. The transition from the α-phase to the fcc δ-phase was observed at about 730 °C. On cooling, similar hysteresis effects as observed in the DTA experiments were encountered. In all experiments performed with a cooling rate of 0.1 °C min^{-1}, the bcc γ-phase was observed at approximately 645 °C. The γ-phase persisted to room temperature, which enabled us to determine the cell dimensions accurately using Si as reference material (see Table 2). On heating the γ-phase, the $\gamma \rightarrow \delta$ transition occurred with a slight hysteresis. Since, in the DTA experiments, the existence of two different intermediate phases was detected around 645 °C, the temperature stability of the Guinier furnace was improved. A number of experimental conditions such as the sample holder material, the cooling rate and the time during which the sample was kept in the δ-phase, were varied. The β-phase was detected in an experiment wherein the sample that had been in the δ-phase for a few minutes only, was cooled at 33 °C min^{-1}. The β-phase could not be preserved to room temperature, but persisted down to approximately 330 °C. The temperature inaccuracy in the Guinier exposures prevented us deciding which of the phases is formed at 650 °C. Structural data of the various phases are given in Table 2.

TABLE 2

STRUCTURAL DATA OF THE Bi_2O_3 PHASES

Phase	*Unit cell*	*a(Å)*	*b(Å)*	*c(Å)*	*β*	*Ref.*	*Notes*
α	Monoclinic	5.848	8.166	7.510	113.00	26	25 °C
		5.843(1)	8.160(1)	7.501(1)	112.92(1)		25 °C
β	Tetragonal	7.73		5.63		7	25 °C from decomposition of bismutite (reduced to primitive cell)
		7.738(3)		5.731(8)			643 °C
γ	bcc	10.268				7	25 °C preserved from high temperature
		10.268(1)					
		10.334(2)					640 °C
δ	fcc	5.66				7	750 °C
		5.644(2)					756 °C

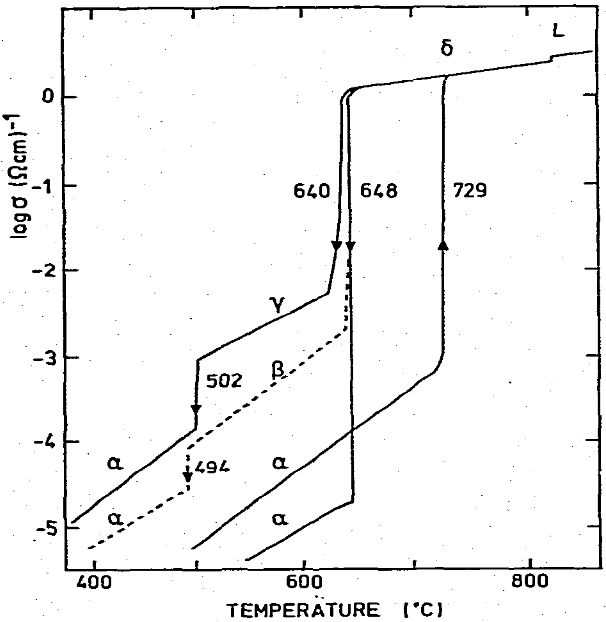


Fig. 5. Electrical conductivity, σ (1592 Hz), of Bi_2O_3 versus temperature. Solid lines, measurements from the liquid state. Broken line, measurement on a compressed powder specimen.

Differential thermal analysis and electrical conductivity measurements

The transitions in Bi_2O_3 were attended by sudden changes in the electrical conductivity. At the $\alpha \rightarrow \delta$ transition, an increase in conductivity of several orders of magnitude was observed in agreement with data by Rao et al.[9] and Takahashi et al.[16] (see Fig. 5). The conductivity in the δ-phase is nearly as high as in the liquid state. In repeated cooling runs from the liquid state, either the β- or the γ-phase appeared. The phase formed at 650(2) °C had a short existence range at low cooling rates, which hampered the measurement of the conductivity in this phase.

The conductivity of both intermediate phases was determined reproducibly on compressed powder specimens supplied with Pt electrodes in an oven with very high temperature stability. Since the phase formed at 640 °C persisted to room temperature, in some of the experiments an unambiguous assignment of the β- and γ-structure to the intermediate phases could be made using X-ray powder diffraction. The DTA peak at 639 °C is associated with the $\delta \rightarrow \gamma$ transition; the peak at 650 °C is associated with the $\delta \rightarrow \beta$ transition. The conductivity data obtained on compressed powder specimens for the γ and δ-phases correspond with the data obtained in measurements cooling from the melt. Representative results of the conductivity measurements are presented in Fig. 5. It is clear that the electronic conductivity of the α-phase is sensitive to the presence of impurities as is reflected in the divergency of the results of various conductivity studies[28].

Differential scanning calorimetry

The transition temperatures and enthalpies obtained in DSC experiments are given in Table 1, together with data from the literature. Using the enthalpy value of

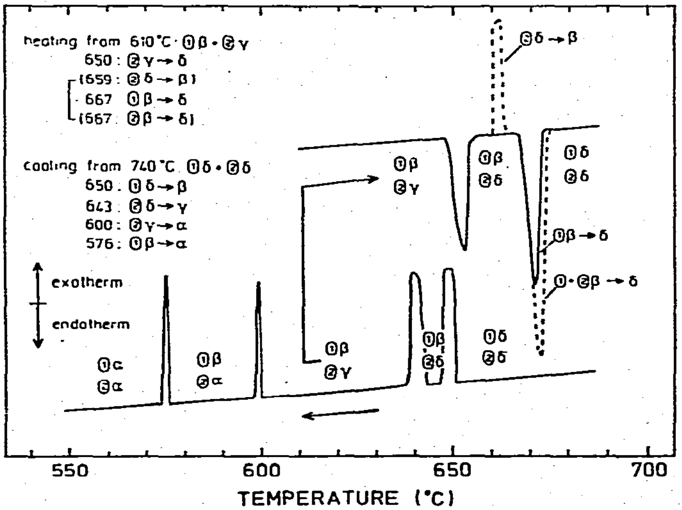


Fig. 6. DSC results for the inhomogeneous Bi_2O_3 sample (see text).

7.06 kcal mole^{-1} for the $\alpha \rightarrow \delta$ transition and the ratio of 2.7 of the DTA peak areas of the $\alpha \rightarrow \delta$ and $\delta \rightarrow$ L transition, the enthalpy of fusion was calculated. The total transition enthalpy on cooling from the δ-phase to the α-phase is approximately 0.14 kcal mole^{-1} smaller than the enthalpy of the $\alpha \rightarrow \delta$ transition. This is due to the large thermal hysteresis and the higher value of the specific heat of the δ-phase compared with the α-phase.

One sample showed a different behaviour on cooling. Two intermediate phases appeared reproducibly in each cooling run (see Fig. 6). This sample consisted of two small lumps of which one transformed reproducibly to the β-phase and the other to the γ-phase on cooling. In heating runs of the inhomogeneous sample from 610°C, where both the β- and the γ-phase were present, the endothermic transition $\gamma \rightarrow \delta$ occurring at 650°C and $\beta \rightarrow \delta$ at 667°C. Frequently, however, the $\gamma \rightarrow \delta$ transition was followed by the exothermic transition $\delta \rightarrow \beta$ in the temperature range 652–660°C, as shown in Fig. 6. This behaviour indicates that the material which showed the γ-phase reproducibly on cooling could exist in the β-phase. The $\delta \rightarrow \beta$ transition in this material is apparently hindered by kinetic effects. Emission spectroscopical analyses revealed substantially different Au and In contents in the two lumps. It is tempting to associate the occurrence of the β-phase with the presence of In.

CONCLUSIONS

Bi_2O_3 may exist in four crystalline modifications. At room temperature, the monoclinic α-phase is the stable form. On heating, the oxide transforms at 729°C to the fcc δ-phase, which is stable up to the melting point at 824°C. On cooling, large thermal hysteresis occurs and two intermediate metastable phases may appear, either the β-phase at 650°C or the γ-phase at 639°C. A survey of the temperature regions in which the stable and metastable phases have been observed is given in Fig. 7.

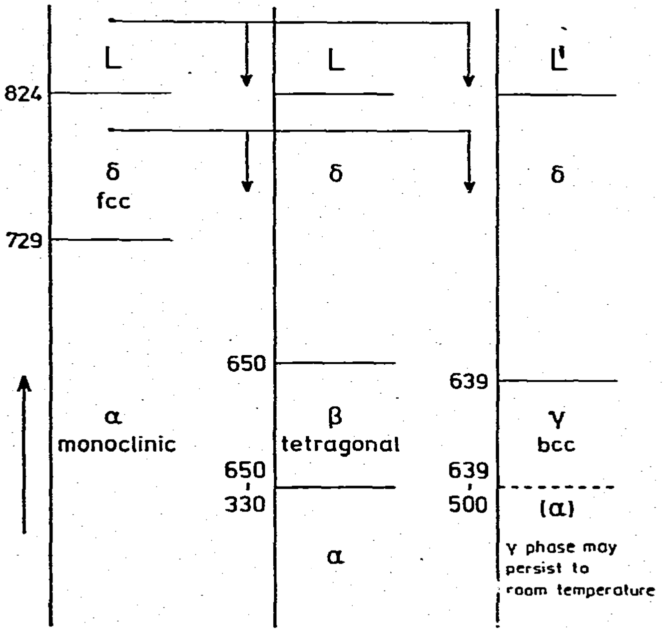


Fig. 7. Survey of the temperature regions of stable and metastable phases encountered in Bi_2O_3.

Which intermediate phase is formed in a particular experiment depends on small amounts of impurities and the texture of the sample.

From the transition enthalpies and temperatures summarized in Table 1, the relative entropy gain at the $\alpha \rightarrow \delta$ transition can be calculated.

$$\frac{\Delta S(\alpha \rightarrow \delta)}{\Delta S(\alpha \rightarrow \delta) + \Delta S(\delta \rightarrow \mathrm{L})} = 0.75$$

Hence the degree of disorder in the δ-phase is comparable with that in the liquid state, a phenomenon which is frequently encountered in fast ionic conductors[29]. The ionic conductivity in the δ-phase is approximately 70–75% of the conductivity in the liquid state. The large thermal hysteresis observed in Bi_2O_3 is another phenomenon which is typical for a compound exhibiting fast ionic conduction in the high temperature phase.

ACKNOWLEDGEMENTS

The authors are indebted to Dr. A. Schuyff of the Laboratory for General Chemistry of the State University Utrecht who kindly permitted us to perform the DSC experiments in his laboratory. Thanks are due to Mr. G. Oversluizen for experimental assistance in the DSC experiments, to Mr. A. Broersma for the TG measurements, and to Mrs. M. Versluys for participation in the X-ray powder diffraction experiments. Dr. J. W. Weenk and Prof. Dr. W. van Gool are gratefully acknowledged for valuable discussions and Dr. T. Harwig for valuable criticism on the manuscript. The investigations have been carried out under the auspices of the Netherlands Foundation of Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of pure Research (ZWO).

REFERENCES

1 W. Guertler, *Z. Anorg. Chem.*, 37 (1903) 222.
2 L. Belladen, *Gazz. Chim. Ital.*, 52 (1922) 160.
3 L. G. Sillén, *Ark. Kemi Mineral. Geol.*, 12A (1937) 1.
4 W. C. Schumb and E. S. Rittner, *J. Am. Chem. Soc.*, 65 (1943) 1055.
5 B. Aurrivillius and L. G. Sillén, *Nature (London)*, 155 (1945) 305.
6 G. Gattow and H. Schröder, *Z. Anorg. Allgem. Chem.*, 318 (1962) 176.
7 E. M. Levin and R. S. Roth, *J. Res. Nat. Bur. Stand. Sect. A*, 68 (1964) 189.
8 G. Gattow and D. Schütze, *Z. Anorg. Allgem. Chem.*, 328 (1964) 44.
9 C. N. R. Rao, G. V. Subba Rao and S. Ramdas, *J. Phys. Chem.*, 73 (1969) 672.
10 R. Matsuzaki, H. Masumizu and Y. Saeki, *Denki Kagaku*, 42 (1974) 578.
11 R. Matsuzaki, H. Masumizu and Y. Saeki, *Bull. Chem. Soc. Jpn.*, 48 (1975) 3397.
12 E. M. Levin and C. L. McDaniel, *J. Res. Nat. Bur. Stand. Sect. A*, 69 (1965) 237.
13 E. M. Levin and C. L. McDaniel, *J. Am. Ceram. Soc.*, 45 (1962) 355.
14 K. K. Kelley, *U.S. Bur. Minus Bull.*, 393 (1936) 25.
15 R. S. Roth and J. L. Waring, *J. Res. Nat. Bur. Stand. Sect. A*, 66 (1962) 451.
16 T. Takahashi, H. Iwahara and Y. Nagai, *J. Appl. Electrochem.*, 2 (1972) 97.
17 T. Takahashi, H. Iwahara, *J. Appl. Electrochem.*, 3 (1973) 65.
18 H. A. Harwig and A. G. Gerards, *J. Solid State Chem.*, in press.
19 H. A. Harwig, *Z. Anorg. Allgem. Chem.*, in press.
20 P. H. Bottelberghs and F. R. van Buren, *J. Solid State Chem.*, 13 (1975) 182.
21 H. von Steinwehr, in H. Geiger and K. Scheel (Eds.), *Handbuch der Physik* Vol. 16, Springer, Berlin, 1927, p. 424.
22 J. I. Langford, *J. Appl. Crystallogr.*, 6 (1973) 190.
23 E. I. Speranskaya, V. M. Skorikov, G. M. Safronov and E. N. Gaidukov, *Inorg. Mater. (USSR)*, 6 (1970) 1201.
24 E. M. Levin and R. S. Roth, *J. Res. Nat. Bur. Stand. Sect. A*, 68 (1964) 197.
25 F. Hund, *Z. Anorg. Allgem. Chem.*, 333 (1964) 248.
26 D. Becherescu, R. Cipau and F. Marx, *Keram. Z.*, 23 (1971) 387.
27 G. Malmros, *Acta Chem. Scand.*, 24 (1970) 384.
28 P. Kofstad, *Nonstoichiometry, Diffusion and Electrical Conductivity in Binary Metal Oxides*, Wiley, New York, 1972, p. 356.
29 W. van Gool, in H. K. Henisch and R. Roy (Eds.), *Phase Transitions*, Pergamon Press, New York, 1973, p. 373.