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STUDY OF THE SYSTEM GeO_2–Bi_2O_3

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ABSTRACT

The stable and metastable equilibrium between GeO_2 and Bi_2O_3 have been studied by DTA and X-ray analysis The three stable compounds, $Bi_2Ge_3O_9$, $Bi_4Ge_3O_{12}$ and $Bi_{12}GeO_{20}$, are formed during exothermic reactions between the starting oxides, when the metastable compound Bi_2GeO_5 is formed only if the melt is cooled from a temperature of ca 50 °C above the liquidus line

INTRODUCTION

Since the first studies of the GeO_2–Bi_2O_3 system [1,2], the existence of two stable compounds and an instable equilibrium were observed Later, Tananaev et al [3] and Zhereb et al [4] have shown that in the Bi_2O_3-rich systems, the structure of the melt is modified by increasing the temperature and that the cooling from a high temperature leads to crystallization of metastable phases Now, four compounds are known in the GeO_2–Bi_2O_3 system (see Table 1)

TABLE 1

Compounds in the system GeO_2–Bi_2O_3

Compound	$Bi_2Ge_3O_9$	$Bi_4Ge_3O_{12}$	Bi_2GeO_5	$Bi_{12}GeO_{20}$
GeO_2 Bi_2O_3 ratio	3 1	3 2	1 1	1 6
Space group	$P6_3/m$	I43d	$CmcZ_1$	I23
System	hexagonal	cubic	orthorhombic	cubic
Cell content	2	4	4	2
Unit-cell dimensions (Å)	$a = 7\ 006$ $b = 9\ 786$	$a = 1\ 053$	$a = 15\ 69$ $b = 5\ 492$ $c = 5\ 383$	$a = 10\ 146$
References	5	6	7	8,9

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We have entered upon a new study of the phase diagram, and the results obtained are consistent with the existence of three stable compounds ($Bi_2Ge_3O_9$, $Bi_4Ge_3O_{12}$ and $Bi_{12}GeO_{20}$) and a metastable compound (Bi_2GeO_5) [10] Recently, a detailed study of this diagram has been published [11] which confirms the existence of the metastable equilibrium and brings forth explanations on many points which were not understood in the previous works

We have also studied the formation of the compounds by means of DTA and X-ray analysis

EXPERIMENTAL

GeO_2 (La Vieille Montagne) and Bi_2O_3 (Johnson Matthey) were mixed in a mortar with acetone, dried and pressed with a pressure of 5 tons cm^{-2} to form cylinders of 3 mm in diameter

Thermal analysis (DTA and TG) were performed at 6 °C min^{-1} with a Mettler TA1, using platinum crucibles, and X-ray analysis with a Guinier-Nonius camera using the Cu K_α radiation

RESULTS AND DISCUSSION

Phase diagram

Figure 1 shows the stable and the metastable diagrams To obtain the stable diagram, we heated the samples at ca 20 °C above the liquidus line, maintained it at this temperature for 10 min and cooled at 6 °C min^{-1}, the determination of the diagram was performed during the second heating If the melt was cooled from a temperature of 50 °C (or more) above the liquidus line the metastable phase diagram was obtained (Fig. 1), which includes three parts

In the middle (near 40% of Bi_2O_3), one obtains on cooling a vitreous solid, which recrystallizes, usually, between 500 and 700 °C to $Bi_4Ge_3O_{12}$, so that we were not able to determine this part of the metastable diagram This phenomenon has been studied by means of high-temperature microscopy by Van Enckevort and Smet [12] Figure 2 shows the DTA of $Bi_4Ge_3O_{12}$ obtained after a first cycle up to 1070 °C, a second up to 1085 °C and a third up to 1100 °C, when the melt is heated to 1100 °C, it does not crystallize during cooling, and we obtain a vitreous solid The decreasing area of the peak is not due to the evaporation of the sample, as is shown by thermogravimetry (Fig 3) It was noted that the weight loss is negligible at 1100 °C The rate of evaporation reaches 0 1 mg min^{-1} at 1350 °C After 10 min at this temperature, the sample has lost ca 10% of its original weight It

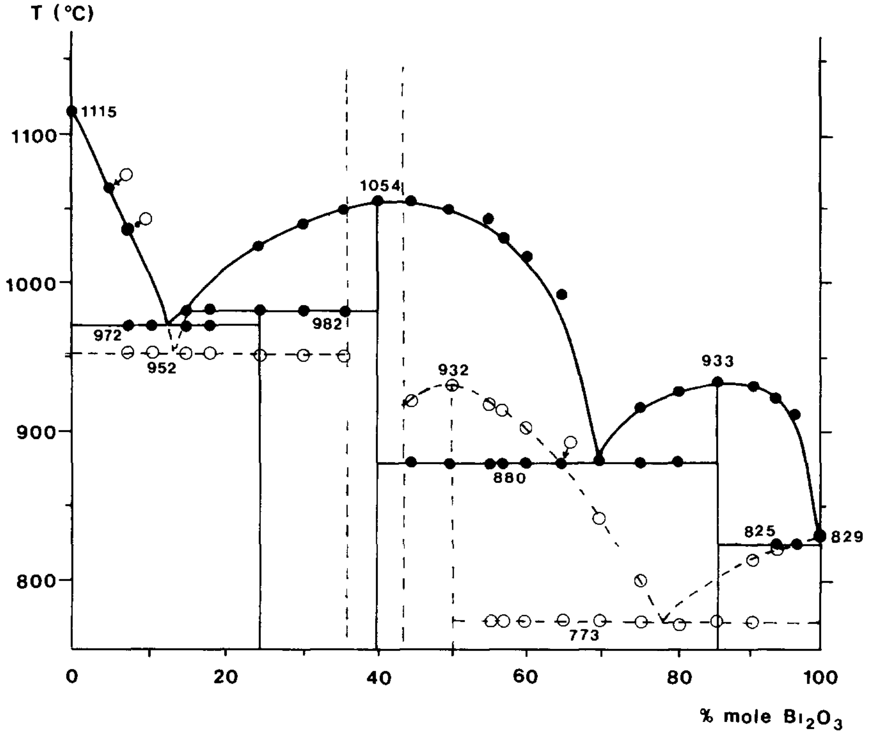

Fig 1 Stable and metastable phase diagram (———) stable, (- - - - - -) metastable

recrystallizes at ca 600 ° C, and we obtain a melting temperature of 1047 ° C, which is very near to that of the starting material $Bi_4Ge_3O_{12}$

At the Bi_2O_3-rich side of the diagram, the metastable compound Bi_2GeO_5 forms a eutectic at 773 ° C with Bi_2O_3 Tananaev et al [3] have postulated a metastable solid solution of GeO_2 in δ-Bi_2O_3, we were not able to detect this solid solution, nor the phase transition of Bi_2GeO_5 at 845 ° C mentioned by Corsmit et al [11], probably on account of the smaller mass of the sample used in our work (10 mg instead of 1 5 g).

At the GeO_2-rich side of the diagram, the compound $Bi_2Ge_3O_9$ did not crystallize and a eutectic forms at 952 ° C between GeO_2 and $Bi_4Ge_3O_{12}$

Formation of the compounds

Table 2 and Fig 4 show the composition range and the temperature of the exothermic peaks observed by DTA during the first heating of the mixture GeO_2–Bi_2O_3

Exotherm at 790 ° C (Fig 5a, b and c)

Between 15 and 96% of Bi_2O_3 we have observed an exothermic reaction at

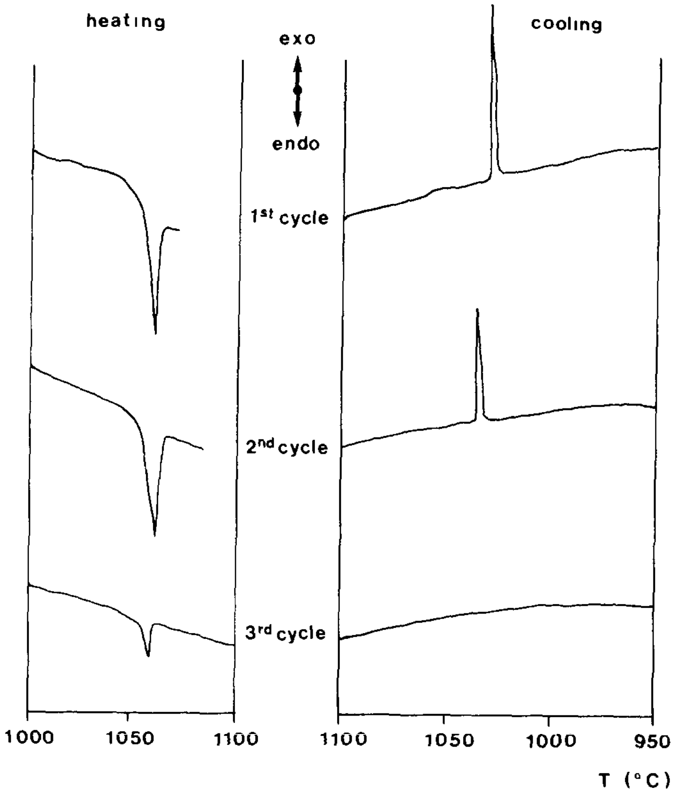

Fig 2 DTA of $Bi_4Ge_3O_{12}$ in air sample weight, 11 7 mg, heating rate, 6 °C min^{-1}

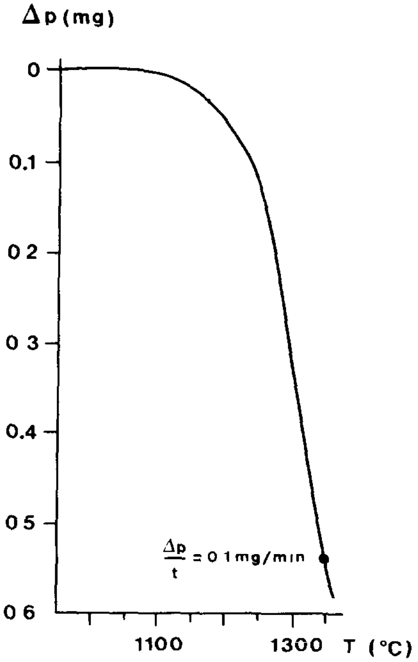

Fig 3 Thermogravimetry of $Bi_4Ge_3O_{12}$ in air sample weight, 9 55 mg, heating rate, 6 °C

TABLE 2

Exothermic peaks observed by DTA

Temperature (° C)	Bi_2O_3 (mol%)	Phases observed [a]
790	10–96	$Bi_{12}GeO_{20}$ [b]
830	7–92	$Bi_{12}GeO_{20}$, $Bi_4Ge_3O_{12}$ [b]
880	78–98	$Bi_{12}GeO_{20}$
950	45–65	$Bi_4Ge_3O_{12}$
960	18–35	$Bi_2Ge_3O_9$

[a] By X-ray analysis Samples are cooled at 100 ° C min^{-1} immediately after the peak GeO_2 and Bi_2O_3 are not mentioned

[b] Another non-identified phase is present between 75 and 90%

790 ° C, due to the formation at $Bi_{12}GeO_{20}$ The intensity of the sharp peak increases with the Bi_2O_3 content

Exotherm at 830 ° C (Fig 5a, b and c)

This temperature corresponds to the melting of Bi_2O_3 The exothermic reaction occurring here leads to the formation of $Bi_{12}GeO_{20}$ and a small quantity of $Bi_4Ge_3O_{12}$, as indicated by X-ray analysis

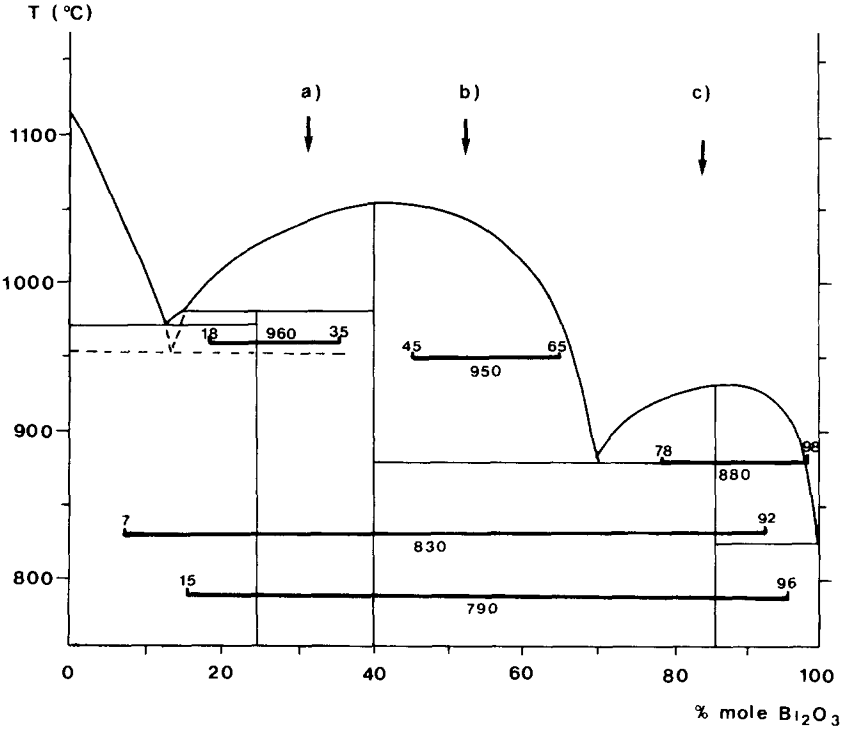

Fig 4 Temperature and composition range of the exothermic effects observed by DTA

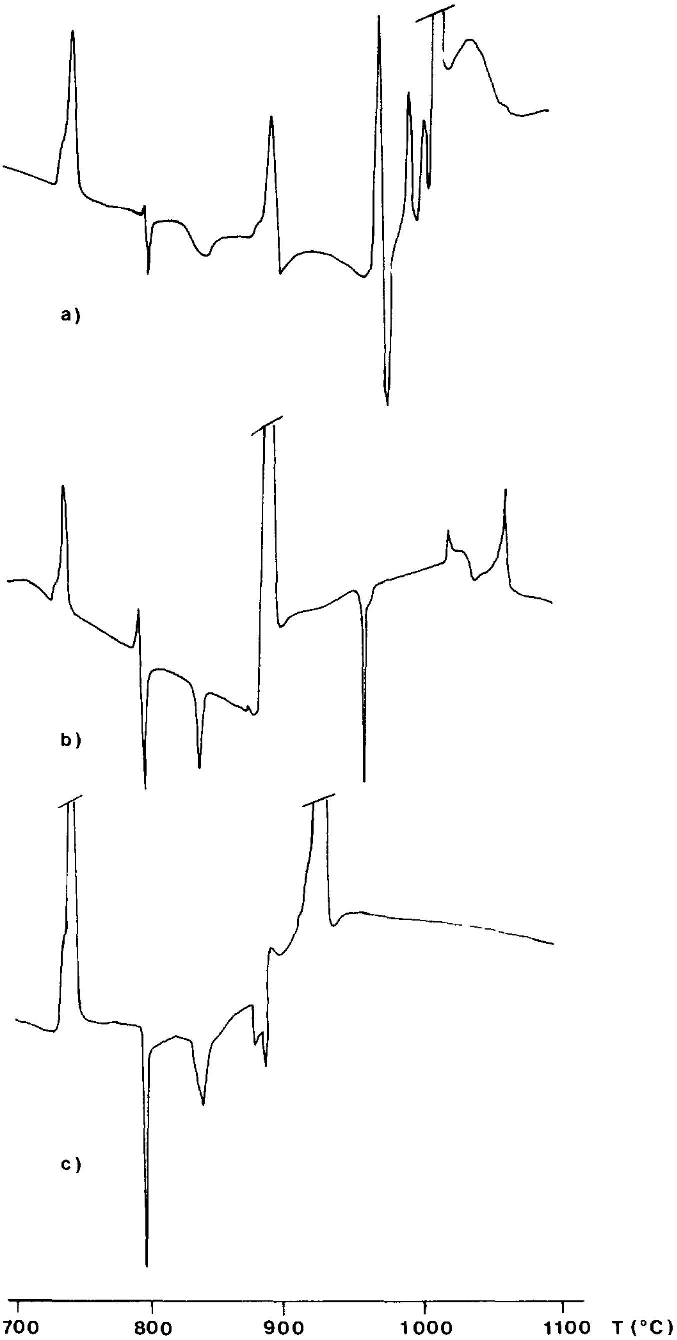

Fig 5 DTA obtained during the first heating sample weight, ca 100 mg, pressed at 5 tons cm^{-2}, heating rate, 6 °C min^{-1} (a) 31 9 mole % of Bi_2O_3 (b) 50 mole % of Bi_2O_3 (c) 85 7 mole % of Bi_2O_3

Exotherm at 880 °C (Fig 5c)

This exothermic peak appears at the Bi_2O_3-rich side of the diagram at the same temperature as the endothermic effect due to the eutectic between $Bi_4Ge_3O_{12}$ and $Bi_{12}GeO_{20}$ After this peak, $Bi_4Ge_3O_{12}$ disappears completely, and the peak probably corresponds to the reaction $Bi_4Ge_3O_{12} + 16\ Bi_2O_3 = 3\ Bi_{12}GeO_{20}$

Exotherm at 950 °C (Fig 5b)

At 950 °C the compound $Bi_{12}GeO_{20}$ transforms to $Bi_4Ge_3O_{12}$

Exotherm at 960 °C (Fig 5a)

This effect follows always an endothermic peak, due to the eutectic between GeO_2 and $Bi_4Ge_3O_9$ It corresponds to the reaction $Bi_4Ge_3O_{12} + 3\ GeO_2 = 2\ Bi_2Ge_3O_9$

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