Thermochimica Acta, 115 (1987) 37–44
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

DERIVATOGRAPHIC INVESTIGATIONS OF THE SYSTEMS $BaO-GeO_2$ AND $BaO-Nb_2O_5$

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(Received 12 September 1986)

ABSTRACT

A range of mixed oxides were prepared by non-isothermal heating of various molar ratios of two binary systems, namely, $BaO-GeO_2$ and $BaO-Nb_2O_5$. In both systems, molten BaO reacts with solid GeO_2 or Nb_2O_5 yielding, respectively, small crystals of various compositions such as $BaGe_4O_9$, $BaGe_3O_7$, $BaGeO_3$, Ba_2GeO_4, $BaGe_3O_5$, and $Ba_4Nb_2O_9$ and $Ba_5Nb_4O_{15}$. All products, except $BaGe_3O_7$, were thermally stable up to the end of the heating program. Both oxides catalytically enhanced the oxidation of BaO to BaO_2. There was no evidence for any discrete identifiable Ba metal. Thermolysis products were mainly identified by X-ray diffractometry.

INTRODUCTION

Studies of phase relations in the systems $BaCO_3-GeO_2$ and $BaCO_3-Nb_2O_5$ by isothermal heating (constant temperature heating) for a relatively long time under atmospheric pressure [1–3] or at high pressures and temperatures [4,5], have been carried out previously. Recently, we have reported [6] the non-isothermal (linear change of temperature) thermoanalytical investigation of $BaO-V_2O_5$ under atmospheric pressure using the TG, DTG and DTA derivatography with promising results; apart from the necessary preparation of large crystals which requires a long time constant, the non-isothermal method is to be preferred to isothermal heating [7]. For reasons mentioned previously [6], and despite their importance as catalysts [8], it seems justifiable to carry out research work on the $BaO-GeO_2$ and $BaO-Nb_2O_5$ systems.

In this paper we report and discuss the TG, DTG and DTA curves obtained for direct high-temperature solid-state reactions of $BaO-GeO_2$ and $BaO-Nb_2O_5$ binary systems and their reaction products.

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0040-6031/87/$03.50

EXPERIMENTAL

GeO_2 (puriss, 99.999%), Nb_2O_5 (puriss, 99.9%), BaO (purum, 99%) were obtained from Fluka. Aluminium oxide (puriss 99.99%; 95% a-form, calcined at 1300 °C, mesh size 0.3 μm, used as a reference material).

Apparatus, procedure and details of preparation of reactants molar ratios and identification of reaction products were described in detail previously [6,9]. Each set of derivatograms (TG, DTG and DTA) documented is the result of two matched pyrolysis replicates using a 200-mg sample in a ceramic crucible (MOM). Platinum crucibles were avoided since the melt sticks strongly to the inner walls on cooling and thus makes it difficult to remove.

RESULTS AND DISCUSSION

Behaviour of GeO_2

Like other semiconductive oxides, the catalytic behaviour of GeO_2 depends in part on whether the lattice structure contains excess Ge (n-type conductor) or is deficient in Ge (p-type semiconductor). The catalytic behaviour is affected at high temperatures, because the lattice structure distorts.

Figure 1 indicates that GeO_2 is thermally stable up to about 950 °C. Above this temperature a loss of about 2 mg per 200 mg sample was observed. The supplied germanium(IV) oxide contains 99.999% GeO_2 and, therefore, this weight loss is not due to a volatile impurity but to a loss of part of the oxide itself.

Behaviour of the $BaO-GeO_2$ system

Prolonged grinding (20 min) with an agate pestle and mortar of molar ratio mixtures of BaO and GeO_2 leads to the air oxidation of the former to BaO_2, which when heated releases oxygen. It seems that GeO_2 catalyses the oxidation process. As can be seen from Fig. 1, a long horizontal plateau (320–400 °C) extends up to the melting point endotherm of BaO. In this range of temperature the previously formed BaO_2 suddenly loses oxygen, $BaO_2 \xrightarrow{\Delta} BaO + \frac{1}{2}O_2$; the amount of BaO formed depends on the proportion of BaO_2 (Table 1) in the mixture. (There is absolutely no evidence to suggest the decomposition of BaO into Ba and O under these experimental conditions.) The amount of oxygen liberated for each molar ratio mixture is summarised in Table 1.

In the melting state ($T_{max} = 370$ °C) BaO reacts with GeO_2 to form the

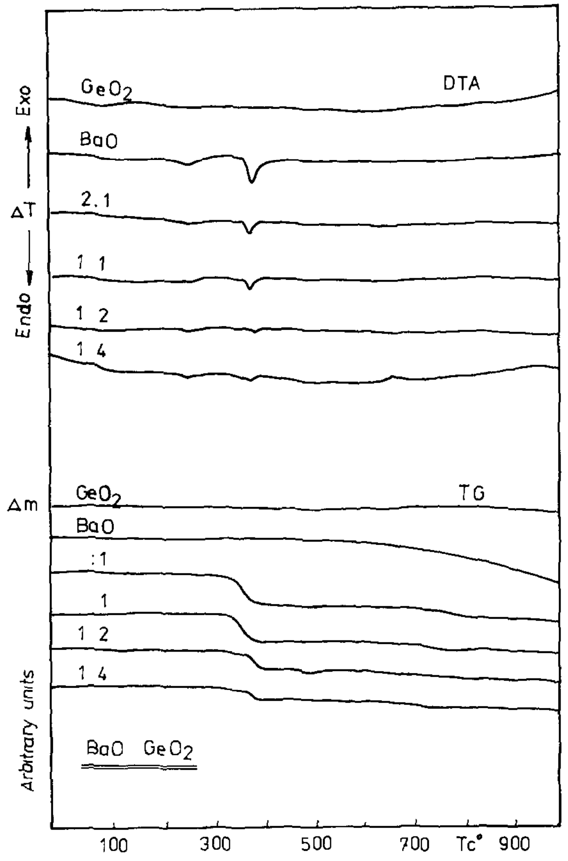

Fig. 1. TG and DTA curves of BaO–GeO_2 mixtures.

unstable mixed oxide, which, according to other findings [4] for $BaGe_3O_7$, follows the reaction equation

$$BaO(l) + 3GeO_2(s) \xrightarrow[370\,^\circ C]{T_{max}} BaGe_3O_7(s)$$

Samples of the 1 : 4 molar ratio mixture heated to 600 °C or above (1000 °C)

TABLE 1

Summary of the preparation and pyrolysis results of the BaO–GeO_2 system

Molar ratio BaO : GeO_2	BaO (mg)	GeO_2 (mg)	Sample weight (mg)	Reaction interval (°C)	T_{max} (°C)	O_2 lost (mg)	Pyrolysis main product
1 : 4	53.68	146.32	200	320–400	370	5.56	$BaGe_3O_7$, $BaGe_4O_9$
1 : 2	84.64	115.36	200	320–400	370	8.50	
1 : 1 [a]	118.95	81.05	200	340–420	370	12.0	$BaGeO_3$ [b]
2 : 1	149.17	50.83	200	320–430	370	15.00	Ba_2GeO_4

[a] Oxygen lost in two steps.

[b] With trace of Ba_2GeO_4.

gave X-ray diffraction (XRD) patterns for two mixed oxides:

$BaGe_2O_5$ [10]			
d-line (Å)	3.68	2.74	2.91
I/I_0	100	100	80
$BaGe_4O_9$ [11]			
d-line (Å)	3.68	2.74	2.91
I/I_0	100	80	60

Moreover, the presence of excess unreacted GeO_2 [12] confirms the validity of the above $BaO:3GeO_2$ reaction ratio for $BaGe_3O_7$ formation which, on disproportionation, results in the production of $2BaGe_3O_7 \xrightarrow{\Delta} BaGe_2O_5 + BaGe_4O_9$.

For other molar ratio mixtures (Table 1), the dominant pyrolysis product was $BaGeO_3$ with a little Ba_2GeO_4. Specimens heated to 600–1000 °C for ratios 1 : 2 and 1 : 1 showed bright *d*-lines for these compounds.

$BaGeO_3$ [12]				
d-line (Å)	3.12	2.20	3.8	3.6
I/I_0	100	50	50	30
Ba_2GeO_4 [14]				
d-line (Å)	3.99	3.06	2.71	3.46
I/I_0	100	100	100	50

The production of $BaGeO_3$ in large quantities from the 1 : 1 ratio mixture is in agreement with the above data.

$$BaO + GeO_2 \xrightarrow{\Delta} BaGeO_3$$

The formation of trace amounts of Ba_2GeO_4 is possibly due to dimerisation and subsequent decomposition of $BaGeO_3$:

$$2BaGeO_3 \xrightarrow{\Delta} Ba_2GeO_4 + GeO_2$$

The appearance of *d*-lines of GeO_2 in the XRD pattern [12] is good evidence for the occurrence of the above reaction. The synthesis yield from the 1 : 1 ratio is greater than for the 1 : 2 ratio and it is expected, therefore, that the former is more stoichiometric than the latter.

X-ray analysis results for $2BaO:GeO_2$ samples heated across the range 550–1000 °C, revealed the formation of Ba_2GeO_4 (main product) in addition to a trace amount of unreacted GeO_2:

$$2BaO + GeO_2 \xrightarrow{\Delta} Ba_2GeO_4$$

Generally, the mixed oxides obtained have different structures and crystalline phases [4] and are thermally stable up to the end of the heating programme (Table 1).

From the above discussion, it seems that it is experimentally possible to synthesise $BaGe_2O_5$, $BaGe_4O_9$ and $BaGeO_3$ by a non-isothermal technique at atmospheric pressure and high temperature.

Behaviour of Nb_2O_5

Nb_2O_5 is an n-type semiconductor; i.e. non-stoichiometric with an oxygen-deficient structure (Nb_2O_{5-x} where $x = 0.1$ at 900 °C). It is thermally stable up to 920 °C above which it decomposes very slightly into NbO_2 and O_2. When hot it assumes a yellow colour; this absorption in the visible region is due to distortion of the unit-cell lattice when the molecules absorb heat energy.

Behaviour of the BaO–Nb_2O_5 system

TG (DTG is not shown for brevity) and DTA curves for the various BaO : Nb_2O_5 molar ratios are shown in Fig. 2. It can be seen that the weight loss (2 mg) represents the liberation of 2 oxygen atoms ($T_{max} = 370$ °C) within the melting endotherm of BaO. The phase change of BaO at 245 °C and its melting endotherm at 370 °C are clearly shown in the curves for the 1 : 4 ratio mixture owing to the relatively small proportion of BaO (Table 2).

An almost similar behaviour was observed for the 2 : 1 ratio except that the weight loss due to the escape of oxygen at 370 °C was 6 mg and 4 mg at 420–540 °C. The liberation of oxygen took place in three consecutive steps whereby the reaction between BaO and Nb_2O_5 continued up to 540 °C. Samples heated to 600–1000 °C gave XRD patterns pertaining to the mixed oxides $Ba_4Nb_2O_9$ which are extremely small green-yellow crystals; the colouration is due to optical and photoelectric effects of high absorbtivity and quantum efficiency.

$Ba_4Nb_2O_9$ [15]

d-line (Å)	2.97	3.295	2.205
I/I_0	100	80	60

in addition of traces of unreacted Nb_2O_5 [16]

d-line (Å)	3.367	3.59	1.91
I/I_0	100	70	50

and $Nb_{12}O_{29}$ [17]

d-line (Å)	3.75	3.616	3.44
I/I_0	100	70	15

The equation for the main yield is, therefore, written as:

$$4BaO + Nb_2O_5 \xrightarrow{\Delta} Ba_4Nb_2O_9$$

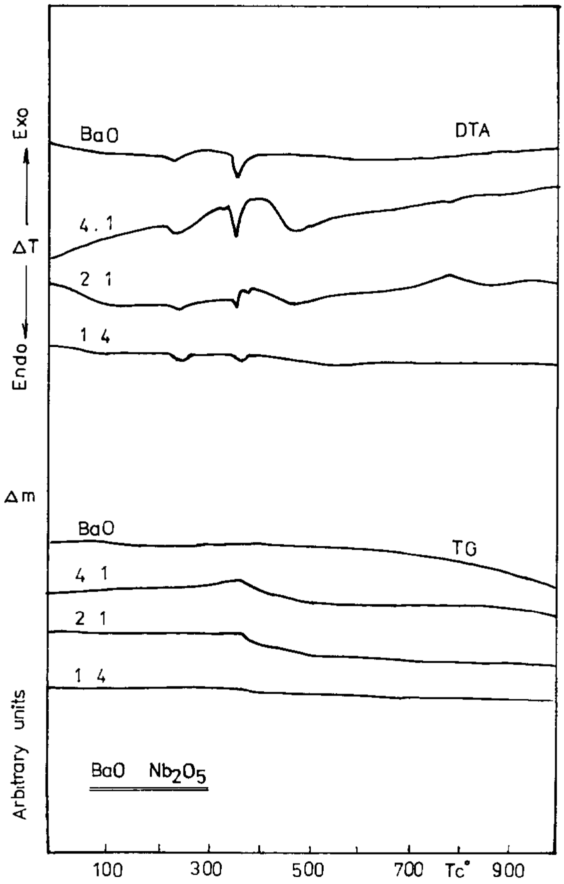

Fig. 2. TG and DTA curves of BaO–Nb_2O_5 mixtures.

The hump-like exo-peak (T_{max} = 783 °C) is due to the slow crystallisation of $Ba_4Nb_2O_9$.

The 4BaO : Nb_2O_5 ratio behaved in a similar fashion to that of the 2 : 1 ratio where the main synthetic product was $Ba_4Nb_2O_9$; in addition, a trace

TABLE 2

Summary of the preparation and pyrolysis results of the BaO–Nb_2O_5 system

Molar ratio BaO : Nb_2O_5	BaO (mg)	Nb_2O_5 (mg)	Sample weight (mg)	Reaction interval (°C)	T_{max} (°C)	O_2 lost (mg)	Pyrolysis main product
1 : 4	25.21	174.79	200	360–420	370	2.00	$Ba_4Nb_2O_9$
2 : 1	107.14	92.86	200	360–420 420–540	370	10.00	$Ba_4Nb_2O_9$
4 : 1	139.53	60.37	200	350–460	370	2.00	$Ba_4Nb_2O_9$

of $Ba_5Nb_4O_{15}$ was detected above 370 °C [18] and when an excess of BaO was present

d-line (Å)	3.09	2.90	2.11
I/I_0	100	100	70

A distinctive feature of the behaviour of this ratio is that the TG curve showed a weight gain (3.50 mg) in the range 200–360 °C due to oxidation of unoxidised BaO; the total BaO in this ratio (Table 2) requires 14.56 mg of oxygen for complete oxidation of BaO to BaO_2. This oxidation process correlates to a small blunt exo-peak on the DTA curve. Surprisingly the hump-like exotherm at 783 °C was not seen for this ratio and instead a small endotherm appeared. No explanation can be offered for this. The $Ba_4Nb_2O_9$ was found to be thermally stable up to the ceiling temperature of the heating programme.

CONCLUSIONS

Almost all the experimental results are summarised in Tables 1 and 2. The curves obtained seem to indicate that molten BaO reacts with solid GeO_2 and Nb_2O_5 in all molar ratios yielding the mixed oxides: $BaGe_4O_9$, $BaGe_3O_7$, $BaGeO_3$, Ba_2GeO_4, $BaGe_3O_5$, $Ba_4Nb_2O_9$ and $Ba_5Nb_4O_{15}$. With the exception of $BaGe_3O_7$, all these compounds are thermally stable.

Prolonged grinding of BaO with individual oxides catalytically enhanced its air oxidation to BaO_2 which at higher temperatures loses oxygen; the amount of BaO_2 formed is proportional to the quantity of BaO present.

In comparison with previous results [4,5] the technique of non-isothermal heating proved to be quite suitable for the preparative chemistry of these compounds.

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