Journal of Thermal Analysis Vol. 33 (1988) 895–901

THERMAL SYNTHESIS OF NON-STOICHIOMETRIC $Bi_{5.8}PO_{11.2}$

D. Schultze

CENTRAL INSTITUTE OF OPTICS AND SPECTROSCOPY, ACADEMY OF SCIENCES OF THE GDR, BERLIN 1199, G.D.R.

The formation of the compound $Bi_{5.8}PO_{11.2}$ from 2.4 $Bi_2O_3 + BiPO_4$ was investigated by means of DTA, simultaneous DTA—high-temperature thermomicroscopy, and X-ray diffraction. Solid-state reactions begin above 700 °C, followed by intermediate local melting and exothermic reactions. These are coupled with the intermediate formation of γ-Bi_2O_3, $Bi_{12}P_{0.8}O_{20}$ (both with sillenite structure) and $Bi_4P_2O_{11}$. The reaction is completed upon congruent melting of $Bi_{5.8}PO_{11.2}$ at 955 °C.

The formation of $Bi_{5.8}PO_{11.2}$ from 2.9 $Bi_2O_3 + NH_4H_2PO_4$ begins after melting of $NH_4H_2PO_4$ at around 200 °C, and is similarly completed at 955 °C.

The compound $Bi_{5.8}PO_{11.2}$, erroneously described by previous authors [1, 2] as Bi_5PO_{10}, has recently been characterized [3] as a stable, congruently melting, non-stoichiometric compound with a very narrow phase width. Honey-yellow single-crystals of this compound can be prepared by pulling from the melt. The starting material for single-crystal growth was synthesized by sintering a mixture of Bi_2O_3 with the calculated amount of either $BiPO_4$ according to

$$2.4\,Bi_2O_3 + BiPO_4 = Bi_{5.8}PO_{11.2} \qquad (1)$$

or $NH_4H_2PO_4$ as described by

$$2.9\,Bi_2O_3 + NH_4H_2PO_4 = Bi_{5.8}PO_{11.2} + NH_3 + 1.5\,H_2O \qquad (2)$$

Equations (1) and (2) give the overall stoichiometry of the reactions. However, the real path of the synthesis is more complex, as demonstrated by DTA, simultaneous DTA—high-temperature thermomicroscopy and X-ray powder diffraction.

Experimental

DTA measurements were performed in equipment consisting of a Chinoin (Budapest) LP 839 temperature programmer, a MOM (Budapest) 4-channel

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

microvolt recorder, and a home-made furnace with specimen holders and Pt/PtRh10 thermocouples. Samples with a mass of 50 mg were placed in covered PtRh10 crucibles. The reference crucible was either empty or contained a weighed amount of potassium sulfate for temperature and enthalpy calibration. Heating rates were usually 10 deg min^{-1}.

For simultaneous DTA–high-temperature thermomicroscopy (HTM), a Carl Zeiss (Jena) horizontal hot-stage microscope MHO was used, modified as described previously [4]. The sample was observed in reflected light at moderate magnification (16 to 24 ×). The control and DTA recording equipment was the same as for the simple DTA equipment.

To characterize intermediate stages in the synthesis, mixtures with the composition formulated in Eq. (1) were heated up to certain temperatures below the melting temperature of $Bi_{5.8}PO_{11.2}$, cooled rapidly to room temperature, and then investigated by means of X-ray powder diffraction in an HZG 4 (Präzisionsmechanik, Freiberg) goniometer and by DTA.

For comparison, other compounds reported in [2] to exist in the Bi_2O_3–$BiPO_4$ section of the Bi_2O_3–P_2O_3 system were prepared through the reaction of well-mixed powders of appropriate amounts of Bi_2O_3 and $NH_4H_2PO_4$ at 700–800°. They were subjected to X-ray diffraction and DTA as well. Finally, model mixtures of presumed intermediates among these compounds were prepared to an overall stoichiometry 5.8 $Bi_2O_3 : 1\ P_2O_5$ and studied by DTA.

Results and discussion

Reaction of starting materials

The DTA diagram of synthesis reaction (1) and the visual changes observed simultaneously via the high-temperature microscope are presented in Fig. 1.

The first strong endotherm (extrapolated onset 726°) indicates the well-known α–δ transformation of Bi_2O_3. Obviously, the synthesis proceeds via several steps. The two-fold appearance of an endotherm immediately followed by an exotherm (at 840–850° and 870–890°) suggests local metastable melting followed by an exothermic reaction, the latter facilitated and accelerated by the increased reactivity of the molten phase. This interpretation is confirmed by the microscopic observation, showing local darkening and/or flashing and disappearance of bright spots. Both phenomena, as experienced earlier, are due to the formation of smaller or larger amounts of a liquid phase. The first-melting phase is probably Bi_2O_3 (m.p. 830°).

The last two endotherms, at (onset) 926° and 947°, correspond to melting of the

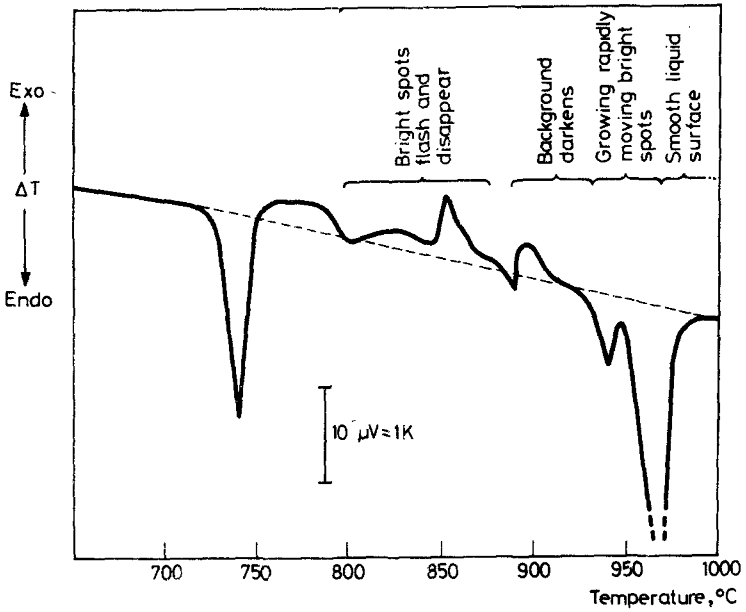

Fig. 1 DTA curve and high temperature thermomicroscopic observations of the mixture 2.4 Bi_2O_3 + $BiPO_4$

eutectic $Bi_{5.8}PO_{11.2}$–$Bi_4P_2O_{11}$ [3] and the final product $Bi_{5.8}PO_{11.2}$, respectively. In this temperature interval the bright spots did not disappear, but remained visible, moving increasingly rapidly and growing until a smooth liquid surface was formed at 959°.

When the same mixture of 2.4 Bi_2O_3 + $BiPO_4$ was investigated by DTA at lower heating rates, the thermal effects became much weaker (except for the last two, due to stable melting). This illustrates the fact that the intermediate steps are non-equilibrium reactions, not going to any stoichiometric completion before the ultimate formation of $Bi_{5.8}PO_{11.2}$.

In the synthesis of $Bi_{5.8}PO_{11.2}$ through reaction (2) (Fig. 2), the first endotherm (onset 210°), due to the melting of ammonium phosphate, is immediately followed by two overlapping exothermic effects, peaking at 282° and 357°. During these exothermic reactions, the majority of the Bi_2O_3 is consumed, as indicated by the very low intensity of the endotherm for the phase transformation α–δ-Bi_2O_3 at 730°. Weak effects slightly above 800° and 900° are again ascribed to metastable melting phenomena. As for reaction (1), the synthesis is concluded by melting of the eutectic $Bi_4P_2O_{11}$–$Bi_{5.8}PO_{11.2}$ and $Bi_{5.8}PO_{11.2}$.

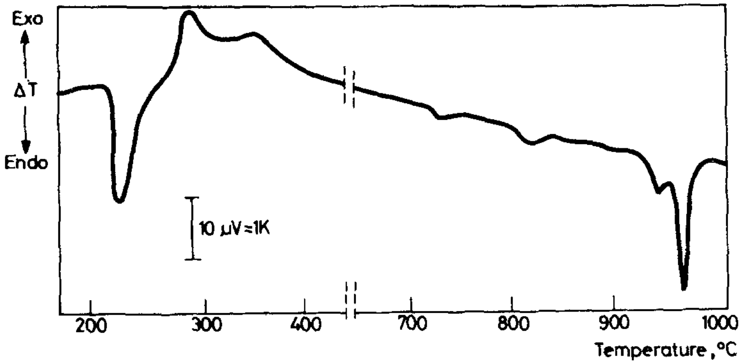

Fig. 2 DTA curve of the mixture 2.9 $Bi_2O_3 + NH_4H_2PO_4$

Study of preheated and quenched intermediates

Mixtures of $BiPO_4 + 2.4\ Bi_2O_3$ were heated at ≈10 deg min^{-1} to 700, 750, 800, 850, 900 and 950°, air-quenched by removal from the furnace, and then studied by means of X-ray diffraction and DTA. The results are compiled in Fig. 3. Up to 700°, no reaction is observed under these conditions. Samples preheated to 750–850° show X-ray diffractograms quite different from those of the starting mixture or the

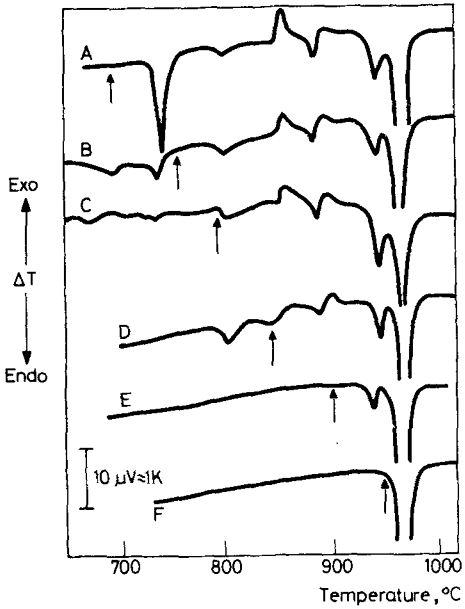

Fig. 3 DTA curves of preheated mixtures 2.4 $Bi_2O_3 + BiPO_4$. Preheating temperatures (marked by arrow): (A) 700, (B) 750, (C) 800, (D) 850, (E) 900, (F) 950 °C

final product $Bi_{5.8}PO_{11.2}$. They could be identified as a mixture of two poorly crystallized cubic sillenite-like phases with lattice constants a_0 = 10.15 and 10.24, probably $Bi_{12}P_{0.8}T\square_{0.2}O_{20}$ [5] and γ-Bi_2O_3. From their relative intensities, it is concluded that, with increasing temperature from 750° to 850°, the content of γ-Bi_2O_3 decreases and that of $Bi_{12}P_{0.8}O_{10}$ increases. Considerations of the reaction stoichiometry lead to the assumption that, besides these sillenite-like phases, another compound must exist, with a higher phosphorus content, but the diffractograms gave no hints on the expectable compounds $BiPO_4$, $Bi_4P_2O_{11}$ or Bi_3PO_7 [2]. Accordingly, it must be assumed that the phosphorus-rich compound is in a rather poorly-crystalline state.

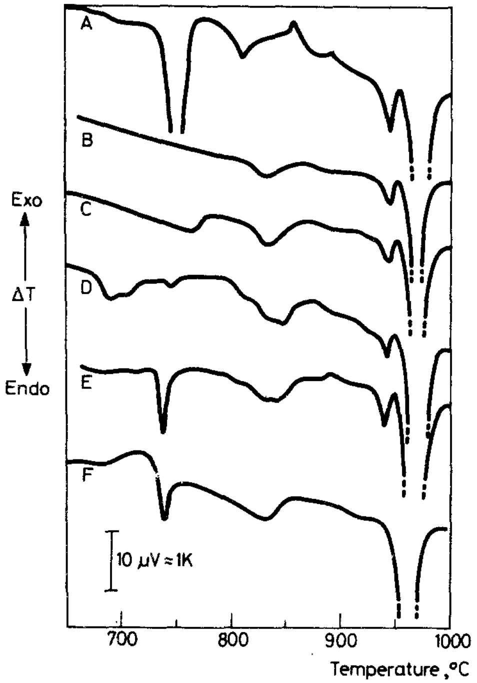

Fig. 4 DTA curves of model mixtures with overall stoichiometry $Bi_2O_3 : P_2O_5$ = 5.8 : 1

curve	component I	component II	molar ratio I : II
A	α-Bi_2O_3	$Bi_4P_2O_{11}$	3.8
B	$Bi_{12}PO_{20.5}$	$BiPO_4$	0.773
C	$Bi_{12}PO_{20.5}$	$Bi_4P_2O_{11}$	1.226
D	$Bi_{25}PO_{40}$ [a]	$BiPO_4$	0.25
E	$Bi_{25}PO_{40}$ [a]	$Bi_4P_2O_{11}$	0.396
F	$Bi_{25}PO_{40}$ [a]	Bi_3PO_7	0.146

[a] The product of this composition, noted by [2] as phase in the system Bi_2O_3–P_2O_5, was in fact a mixture of $Bi_{12}P_{0.8}O_{20}$ and γ-Bi_2O_3, both of sillenite structure.

The diffractograms of the sample preheated to 900° shows a mixture of the final product $Bi_{5.8}PO_{11.2}$ and traces of $Bi_4P_2O_{11}$. Correspondingly, the DTA curve exhibits the endothermic peaks of melting of the respective eutectic and the final product. The mixture preheated to 950° gives the single melting endotherm of pure $Bi_{5.8}PO_{11.2}$ and the X-ray diffractogram of this compound only.

Study of model mixtures

To elucidate the nature of the phosphorous-rich compound postulated as an intermediate above, model mixtures with Bi : P ratio 5.8 : 1 were prepared from the various bismuth phosphate compounds described in the Bi_2O_3–P_2O_5 system. From their DTA curves (Fig. 4), only those of mixtures containing $Bi_4P_2O_{11}$ show some similarity with the DTA curves of mixtures of 2.4 $Bi_2O_3 + BiPO_4$ preheated to 750–850°. This result, together with the detection of traces of $Bi_4P_2O_{11}$ by X-ray diffractometry, allow the conclusion that $Bi_4P_2O_{11}$ plays a role as an intermediate in the synthesis of $Bi_{5.8}PO_{11.2}$.

Conclusions

The synthesis of $Bi_{5.8}PO_{11.2}$ from $BiPO_4 + 2.4$ Bi_2O_3 occurs in several steps, beginning as a solid-state reaction and accelerated by partial melting due to the occurrence of metastable eutectics. Two sillenite-like phases, viz. $Bi_{12}P_{0.8}O_{20}$ and γ-Bi_2O_3, the latter probably stabilized by a smaller content of phosphorus, most likely together with $Bi_4P_2O_{11}$, are formed as intermediates during the synthesis reaction. Thus, the synthesis proceeds via the formation of compounds with Bi : P ratios lying between those of the starting materials (1 : 1 and 1 : 0, respectively) and the final product.

The reaction of Bi_2O_3 with $NH_4H_2PO_4$ to $Bi_{5.8}PO_{11.2}$ starts at a much lower temperature, immediately after the melting of ammonium phosphate.

* * *

Thanks are due to Mrs. K. Norouzi for performing most of the DTA measurements, and to Mr. P. Höfner for the recording and discussions of the X-ray diffractograms.

References

1 L. H. Brixner and C. M. Foris, Mater. Res. Bull., 8 (1973) 1311.

2 V. V. Volkov, L. A. Zhareb, J. F. Kargin, V. M. Skorikov and I. V. Tananaev, Zh. Neorg. Khim., (Russ) 28 (1983) 1002.

3 D. Schultze and R. Uecker, Thermochim. Acta, 93 (1985) 509.

4 D. Schultze, Thermochim. Acta, 29 (1979) 233.

5 M. Devalette, G. Meunier, J.-P. Manaud and P. Hagenmuller, C. R. Acad. Sc. Paris Serie II, 296 (1983) 189.

Zusammenfassung — Die Bildung der Verbindung $Bi_{5.8}PO_{11.2}$ aus 2,4 $Bi_2O_3 + BiPO_4$ wurde mittels DTA, simultaner DTA-Hochtemperatur-Thermomikroskopie und Röntgenbeugung untersucht. Die Umsetzung beginnt als Festkörperreaktion oberhalb 700 °C, gefolgt durch intermediäres örtliches Schmelzen und exotherme Reaktionen. Dabei werden als Zwischenprodukte γ-Bi_2O_3, $Bi_{12}P_{0,8}O_{20}$ (beide mit Sillenit-Struktur) sowie $Bi_4P_2O_{11}$ nachgewiesen.. Die Umsetzung wird erst beim kongruenten Schmelzen des $Bi_{5,8}PO_{11,2}$ bei 955 °C beendet. Die Bildung von $Bi_{5,8}PO_{11,2}$ aus 2,9 $Bi_2O_3 +$ $NH_4H_2PO_4$ beginnt nach dem Schmelzen des $NH_4H_2PO_4$ bei ca. 200 °C und geht ebenfalls erst bei 955 °C zu Ende.

Резюме — Методом ДТА, совмещенным методом ДТА и высокотемпературной термомикроскопии и рентгенофазовым анализом изучено образование соединения $Bi_{5.8}PO_{11.2}$ из смеси 2,4 Bi_2O_3 и $BiPO_4$. Твердотельные реакции начинаются выше 700° и сопровождаются локальным плавлением и экзотермическими эффектами, что связа — с образовением промежуточных продуктов β-Bi_2O_3, $Bi_{12}P_{0,8}O_{20}$ (оба соединения со структурой силленита) и $Bi_4P_2O_{11}$. Реакция заканчивается конгруэнтным плавлением $Bi_{5,8}PO_{11,2}$ при 955°. Образование соединения из смеси 2,9 Bi_2O_3 и $NH_4H_2PO_4$ начинается после плавления кислого фосфата аммония при температуре около 200° и заканчивается подобно предыдущему при 955°.