Journal of Thermal Analysis, Vol. 52 (1998) 481-488

FORMATION AND THERMAL DECOMPOSITION OF INDIUM OXYNITRIDE COMPOUNDS

A. Tokarzewski and S. Podsiadlo

Department of Chemistry, Warsaw Institute of Technology, Noakowskiego 3, 00644 Warsaw
Poland

(Received February 7, 1997; in revised form May 9, 1997)

Abstract

During the reactions of lithium oxide with indium nitride, lithium nitride with indium oxide, and lithium nitride with lithium indate $LiInO_2$, the formation of a previously unknown crystalline phase, of composition Li_4InNO_2, was observed. The course of thermal decomposition of the new compound was determined.

Keywords: indium nitride, indium oxide, lithium oxide, lithium nitride, lithium indate, reactivity

Introduction

In earlier works concerning the reactivity of BN, AlN and Si_3N_4 with Li_2O and Na_2O, the existence of the anions BNO^{2-}, $AlNO^{2-}$, $SiNO^-$, $SiNO_2^{3-}$, $SiNO_3^{5-}$ and $SiN_2O_2^{6-}$ in the form of lithium and sodium salts was found [1–6]. Since compounds with a mixed oxynitride coordination shell round the central element are known in the chemistry of Al, Si and Ge [7–11], it seemed reasonable that In, situated in the same area in the periodic system, may also form such salt. The discussion of the results is based on the morphological classification of simple species modified for heteroligand bonding [2, 7]. The transformations of the species taking part in the reactions may be presented in a classification table within the $e_z(O^{2-})$–$e_z(N^{3-})$ coordinate system, where $e_z(O^{2-})$ denotes the number of electrons introduced by oxygen ligands to the coordination center for the formation of σ bonds, and $e_z(N^{3-})$ denotes the number of electrons introduced by nitrogen ligands to the coordination center for the formation of σ bonds.

Pure nitride species of In lie on the line, $e_z(O^{2-})=0$, and species with pure oxide coordination shells lie on the line $e_z(N^{3-})=0$. For example:

InN	$e_z(O^{2-}) = 0$;	$e_z(N^{3-}) = 2$
In_2O_3	$e_z(O^{2-}) = 3$;	$e_z(N^{3-}) = 0$
$InNO_2^{4-}$	$e_z(O^{2-}) = 4$;	$e_z(N^{3-}) = 2$
$InNO^{2-}$	$e_z(O^{2-}) = 2$;	$e_z(N^{3-}) = 2$

1418–2874/98/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

The addition of an oxide ligand causes an increase in the $e_z(O^{2-})$ number, and that of a nitride ligand causes a corresponding increase in the $e_z(N^{3-})$ number. Besides the classification of the structures, this table permits a presentation of the transformations of the particular species.

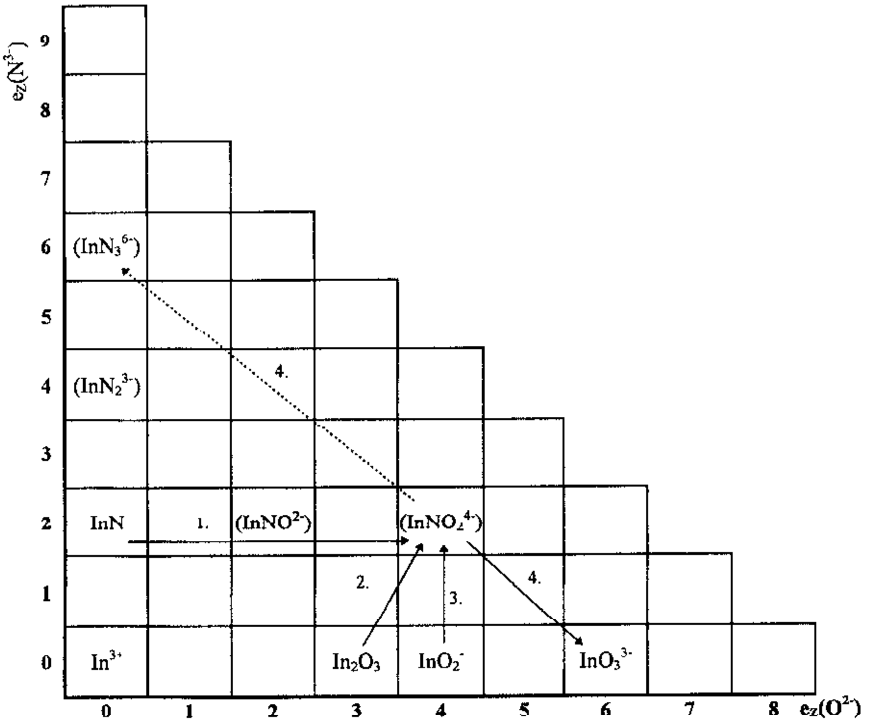

Fig. 1 Classificational table of oxynitride compounds of In (hypothetical species in parentheses)

Figure 1 shows a classification table in the system of axes $e_z(O^{2-})$–$e_z(N^{3-})$, which presents the known In oxy compounds, In compounds with a nitride coordination shell, and hypothetical In compounds with mixed oxynitride coordination shells (in parentheses).

Experimental

The courses of the reactions were studied by thermal analysis on a MOM derivatograph (Budapest, Hungary). The syntheses at characteristic temperatures were carried out in tube furnaces under nitrogen atmosphere. The reaction products were studied, after freezing, by X-ray phase analysis (HZG4 apparatus, Freiberger Prezision Mechanik, Germany), IR absorption of solid products (Specord, Carl Zeiss, Jena, Germany) and quantitative analysis.

The following substances were used in the work: indium nitride InN, produced in our laboratory [12]; lithium oxide, Li_2O, analytical grade produced by Merck (Germany); indium oxide, In_2O_3, synthesized in our laboratory; and lithium indate, $LiInO_2$, produced in our laboratory.

Results and discussion

Figure 2 shows TG and DTA curves of a 1:1 molar mixture of InN with Li_2O in nitrogen atmosphere.

At 230 and 450°C, weak exothermic effects with no accompanying loss of mass are observed. X-ray diffraction studies on the products of the reaction up to 600°C show that they are amorphous. Above 600°C, mass loss is observed, reaching a value of 6.6% at 650°C. At this temperature, a solid product is obtained with a composition corresponding to a mixture of Li_2O, lithium indate $LiInO_2$, lithium indate Li_3InO_3 and free In, all in crystalline form [13, 14].

At 860°C, the mixture contains Li_2O, Li_3InO_3 and free In.

Figure 3 presents thermal curves of a 1:2 molar mixture of InN with Li_2O in nitrogen atmosphere.

At 220 and 460°C, weak exothermic effects with no accompanying mass loss are observed. X-ray diffraction examination of the product of the reaction at 230°C shows the presence of substrates InN and Li_2O. The solid product of the reaction at 480°C contains In and Li_2O, and three peaks of an unknown crystalline phase are also observed (its X-ray diffraction data are given in Table 1).

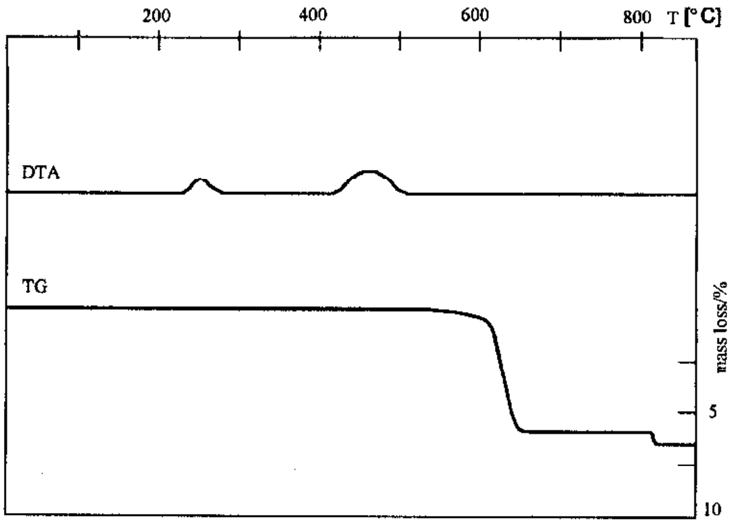

Fig. 2 Thermogravimetric analysis of mixture of InN with Li_2O (molar ratio 1:1), m=0.159 g, β=4.0°C min^{-1}, N_2

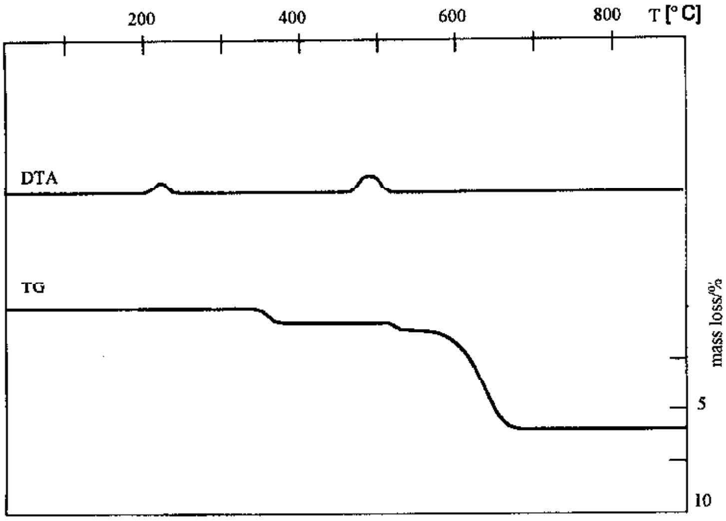

Fig. 3 Thermogravimetric analysis of mixture of InN with Li_2O (molar ratio 1:2), m=0.155 g, β=4.0°C min^{-1}, N_2

At 600°C, loss of mass starts, reaching 5.9% at 680°C. The product of the reaction at this temperature contains (after freezing): InN, Li_2O, Li_3InO_3 and In, all in crystalline form, and a new, hitherto unknown crystalline phase [13, 14] (its X-ray diffraction data are given in Table 1).

Table 1 X-ray diffraction data of new phase – product of the reaction of InN+2Li_2O at 600°C (other products are Li_3InO_3, $LiInO_2$ and InN)

d/[pm]	462.3	332.7	153.0	147.3	139.3	138.4
I/I_0	100	40	15	15	10	25

The products of the reaction at 900°C consist of Li_2O, Li_3InO_3 and In.

The total mass loss in the reaction up to 900°C is 5.9%, the theoretical loss of mass connected with evaporation of all nitrogen being 7.4%. This shows that part of the nitrogen used in the reagents is bonded in the products at 900°C. The elemental analysis confirms this. The mixture of products probably also contains amorphous alloys of Li and In [15].

Figure 4 shows thermal curves of 2:1 molar mixture of Li_3N with In_2O_3 in nitrogen atmosphere.

At 320°C a weak endothermic effect, and at 400°C a weak exothermic effect with no loss of mass are observed. X-ray diffraction studies of the reaction at 400°C showed the presence of Li_3N and In_2O_3. X-ray analysis of the product obtained in a tube of furnace at 460°C revealed the formation only the crystalline phase identified in the former experiment as a product of the reaction of InN with Li_2O (see X-ray diffraction data in Table 1) and metal In.

At 480°C, an exothermic effect is observed, accompanied by a small loss of mass (1.4%). The next exothermic effect at 580°C is strong and the mass loss at

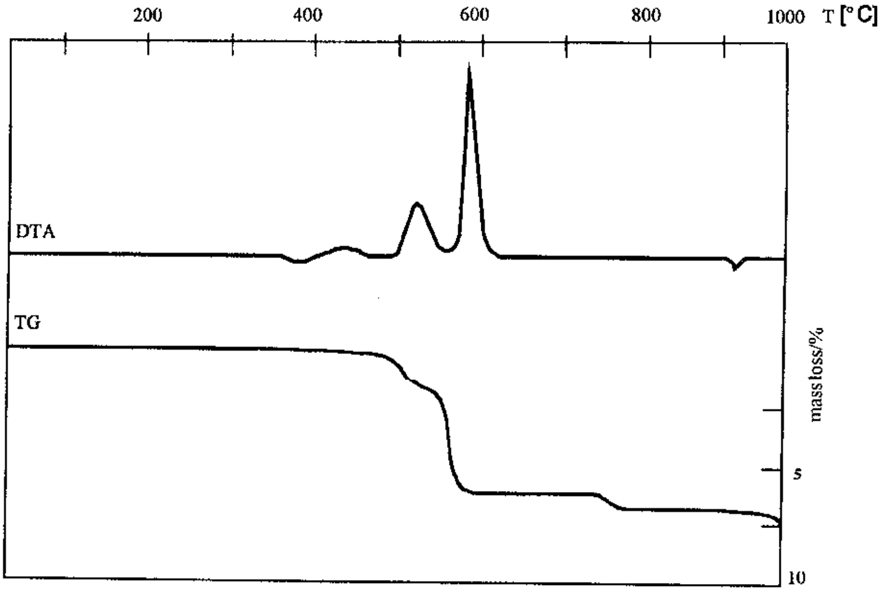

Fig. 4 Thermogravimetric analysis of mixture of In_2O_3 with Li_3N (molar ratio 1:2), m=0.201 g, β=9.0°C min^{-1}, N_2

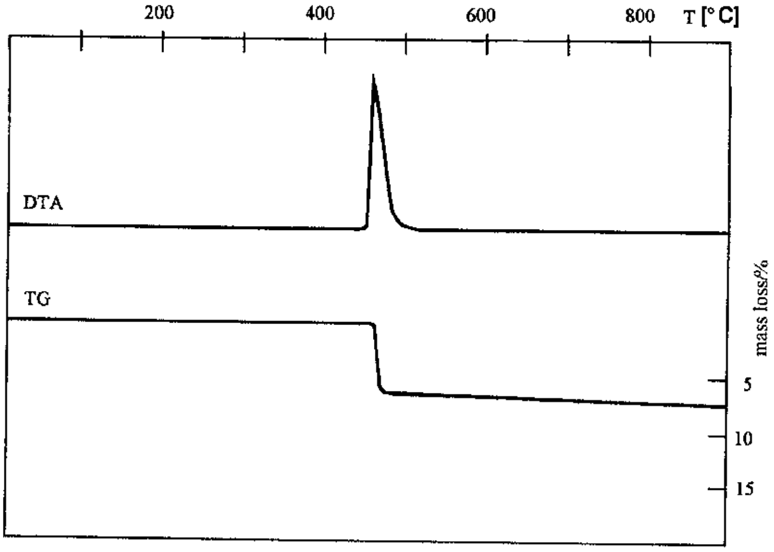

Fig. 5 Thermogravimetric analysis of mixture of $LiInO_2$ with Li_3N (molar ratio 1:1), m=0.127 g, β=9.0°C min^{-1}, N_2

this temperature reaches 6.8%. X-ray analysis of the products of the reaction at 580°C showed the presence of $LiINO_2$, Li_3InO_3, In and Li_2O. At 760°C, we can observe a small loss in mass (about 0.7%) and the products at 900°C are Li_3InO_3 and In, both identified by X-ray diffraction analysis (after freezing).

The total mass loss in the reaction up to 900°C is 3.3% and the theoretical contamination of nitrogen in the sample is 4.5%. This shows that part of the nitrogen involved in the process is bonded in the products at 900°C. This was confirmed by elemental analysis [16]. The mixture of products presumable also contains amorphous alloys of Li and In [15].

Figure 5 presents TG and DTA curves of a 1:1 molar mixture of $LiInO_2$ with Li_3N in nitrogen atmosphere.

Up to 450°C, there are no thermal effects or mass loss. However X-ray diffraction analysis showed that at 250°C a crystalline phase was formed. This is the same compound as that obtained in the reactions of InN with Li_2O (molar ratio 1:2) and of In_2O_3 with Li_3N (molar ratio 1:2). X-ray diffraction data for identification of this phase are given in Table 1. Small quantities of $LiInO_2$ are also identified by the X-ray method in the product of the reaction. This phase, in this system, is stable up to 470°C. The IR spectrum of the new phase is given in Fig. 6. This spectrum does not contain absorption bands characteristic of In_2O_3, InN, Li_3N or $LiInO_2$.

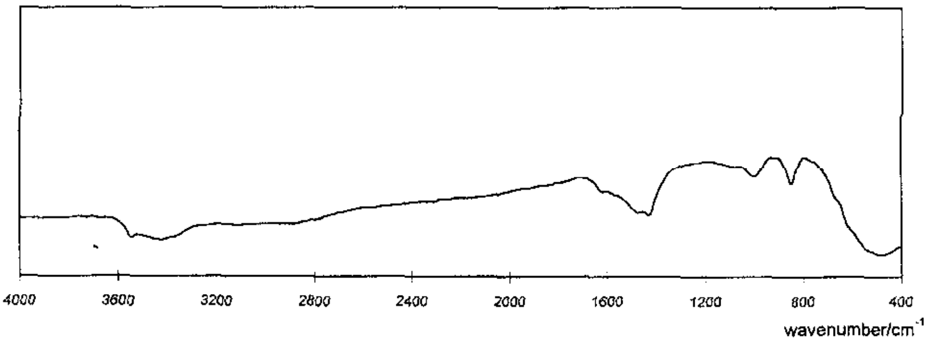

Fig. 6 IR spectrum of Li_4InNO_2

Elemental analysis reveals that the new phase has the stoichiometry Li_4InNO_2.

At 470°C, we observe a strong exothermic effect and a mass loss (6.3%). The products of this thermal decomposition contained Li_3InO_3 and In. The overall loss in mass in the reaction up to 700°C is 6.3% and the theoretical contamination of nitrogen in the sample is 7.8%. This shows that part of the nitrogen used in the process is bonded in the products at 600°C. This was confirmed by elemental analysis [16]. The mixture of products presumably also contains alloys of Li and In [15].

The following conclusions may be drawn:

– In the reaction of InN with Li_2O (molar ratio 1:2), the new crystalline compound Li_4InNO_2 is formed at 480°C:

$$2Li_2O + InN \rightarrow Li_4InNO_2 \tag{1}$$

– The same crystalline phase is formed in the reaction of In_2O_3 with Li_3N (molar ratio 1:2) at 460°C:

$$2In_2O_3 + 4Li_3N \rightarrow 3Li_4InNO_2 + In + N_2 \tag{2}$$

– In the reaction of $LiInO_2$ with Li_3N (molar ratio 1:1), Li_4InNO_2 is obtained at 250°C:

$$2LiInO_2 + Li_3N \rightarrow Li_4InNO_2 \tag{3}$$

The pathways of these reactions are very clearly shown in the classification table in Fig. 1 (the numbers of the reactions correspond to those of the transformations in the classification table).

Analogously to the postulated compound, the B and Al compounds Li_2BNO [1] and Li_2AlNO [2] are formed in the reactions

$$Li_2O + BN \rightarrow Li_2BNO$$

$$Li_2O + AlN \rightarrow Li_2AlNO$$

and their thermal decompositions proceed as follows [1, 2]:

$$2Li_2BNO \rightarrow LiBO_2 + Li_3BN_2$$

$$2Li_2AlNO \rightarrow LiAlO_2 + AlN + Li_3N\uparrow$$

If the thermal decomposition of the new compound (Li_4InNO_2) obtained in our investigation takes place in a similar way, as is known in Si chemistry, when two products with uniform coordination shells are formed from compounds with a mixed oxynitride coordination shell, this could be considered additional proof of the existence of Li_4InNO_2. The results presented earlier suggest that the thermal decomposition of this salt proceeds as follows:

$$3Li_4InNO_2 \rightarrow 2Li_3InO_3 + Li_6InN_3 \text{ (unknown)} \tag{4}$$

$$Li_6InN_3 \rightarrow Li_{6-x}In_{1-y}N_z + Li_xIn_y + ((3/2 - z/2)N_2)$$

The numerals ascribed to these reactions correspond to the numerals denoting the transformations in the classification table (Fig. 1).

The fact that the decomposition of the oxynitride salt of In does not proceed identically, but only similarly as in the chemistry of Al, Si and Ge [17], results from the differences in the thermal stabilities of Li_3AlN_2, compounds in the Li–In–N system, compounds in the Li–Ge–N system and so far unknown compounds in the Li–In–N systems.

During the investigation of the system Li–In–N, we have found a few previously unknown crystalline phases. This complex problem will be the subject of our next paper.

References

1 S. Podsiadlo and B. Rodzen, Polish J. Chem., 58 (1984) 643.
2 Z. Lapinski and S. Podsiadlo, J. Thermal Anal., 32 (1987) 49.
3 S. Podsiadlo, J. Thermal Anal., 32 (1987) 43.
4 S. Podsiadlo, J. Thermal Anal., 32 (1987) 445.
5 S. Podsiadlo, J. Thermal Anal., 32 (1987) 771.
6 A. Krasnicka and S. Podsiadlo, J. Thermal Anal., 34 (1988) 305.
7 S. Podsiadlo, Polish J. Chem., 58 (1984) 643.
8 S. Podsiadlo, Polish J. Chem., 58 (1984) 653.
9 Y. Laurent, F. F. Grekov, J. David and J. Guyader, Ann. Chim. France 5 1980) 647.
10 J. Guyader, J. Malharie and Y. Laurent, Rev. Chim. Min., 19 (1982) 701.
11 J. Guyader, R. Jacquet, J. Malharie, G. Roult and Y. Laurent, Rev. Chim. Min., 20 (1983) 863.
12 S. Podsiadlo, Thermochim. Acta, 256 (1995) 375.
13 Powder Diffraction Structure Database, DHN, Wroclaw, Poland, 1992.
14 Inorganic Crystal Structure Database, Gmelin, FIZ, Karlsruhe, 1995.
15 Gmelin, Handbuch der anorganischen Chemie, Gallium, Berlin 1991, Vol. 36, Verlag Chemie, p. 58.
16 S. L. Ericson and F. J. Conrad, Talanta, 18 (1971) 1066.
17 S. Podsiadlo, J. Thermal Anal., 34 (1988) 983.