Journal of Thermal Analysis and Calorimetry, Vol. 61 (2000) 873–877

FORMATION AND THERMAL DECOMPOSITION OF GALLIUM OXYNITRIDE COMPOUNDS

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(Received February 10, 1999)

Abstract

The formation of a previously unknown crystalline phase was observed in the system Li–Ga–N–O. During the reactions of Ga_2O_3 with Li_3N and of $LiGaO_2$ with Li_3N, a new compound with the stoichiometry Li_4GaNO_2 was formed. The stages in thermal decomposition of the new phase were determined.

Keywords: gallium nitride, gallium oxide, lithium gallate, lithium nitride, lithium oxide, reactivity

Introduction

Earlier work on the formation of compounds containing a mixed nitrooxy coordination shell demonstrated the existence of Li_2BNO, Na_2BNO, Li_2AlNO, $LiSiNO$, Li_3SiNO_2, Li_4InNO_2, etc [1–7]. It was suggested that such compounds can also be prepared for gallium, an element lying close to aluminum, silicon and indium in the periodic table of elements. The results were discussed on the basis of the morphological classification for simple species modified for heteroligand bonding [4]. The species and their transformations in the reactions were presented in a classification system with $e_z(O^{2-})$ and $e_z(N^{3-})$ on the axes. The parameter $e_z(O^{2-})$ denotes the number of electrons introduced by the oxygen ligands to the coordination center for the formation of sigma bonds, and parameter $e_z(N^{3-})$ denotes the number of electrons introduced by the nitrogen ligands to the coordination center for the formation of sigma bonds [4].

Species with purely oxide coordination shells around the gallium lie on the line $e_z(N^{3-})=0$, while pure nitride species of gallium lie on the line $e_z(O^{2-})=0$, e.g:

Ga_2O_3 $e_z(O^{2-})=3$; $e_z(N^{3-})=0$
GaN $e_z(O^{2-})=0$; $e_z(N^{3-})=2$
$GaNO_2^{4-}$ $e_z(O^{2-})=4$; $e_z(N^{3-})=2$
$GaNO^{2-}$ $e_z(O^{2-})=2$; $e_z(N^{3-})=2$

The introduction of an oxide ligand into the coordination environment of the gallium increases $e_z(O^{2-})$, and that of a nitride ligand results in a corresponding in-

1418–2874/2000/ $ 5.00

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crease in $e_z(N^{3-})$. Besides the classification of the species, this system also permits a presentation of their transformations.

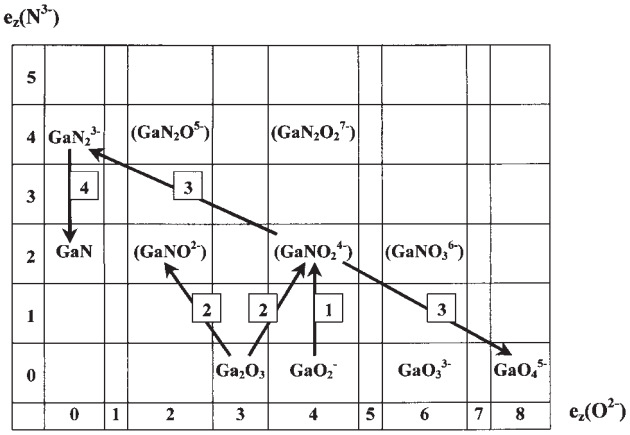

Fig. 1 Classification of gallium oxynitride compounds

Figure 1 provides a classification of known gallium oxy compounds, known gallium nitro compounds, and hypothetical gallium oxynitride compounds (in parentheses).

Experimental

Initial examinations of the reaction courses were carried out by thermal analysis on a MOM derivatograph (Budapest, Hungary). Syntheses at some characteristic temperatures were carried out in tube furnaces under a nitrogen atmosphere. The products obtained were studied, after cooling, by means of X-ray diffraction (apparatus HZG-4, Freiberger Prezision Mechanik, Germany), infrared absorption of the solid products (Specord, Carl Zeiss Jena, Germany) and quantitative analyses.

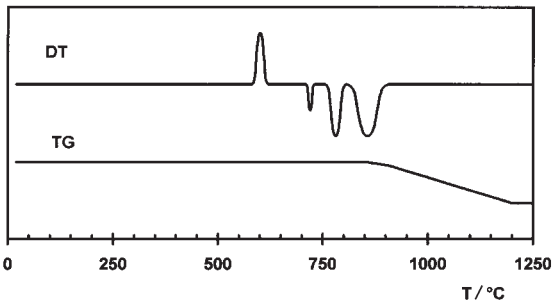

Fig. 2 TG and DTA curves of a mixture of Li_3N with Ga_2O_2 (molar ratio 2:1), m=0.152 g, β=4°C min^{-1} (N_2)

The following reactants were used in the studies: gallium nitride [8], lithium nitride, gallium oxide and lithium gallate, all produced in our laboratory; lithium oxide, analytical grade, produced by Merck (Germany).

Results and discussion

The TG and DTA curves of a 2:1 molar mixture of Li_3N with Ga_2O_3 in nitrogen atmosphere are presented in Fig. 2.

A strong exothermic effect with no loss in mass is observed at 600°C. X-ray analysis of the products of this step of the reaction revealed the formation of a previously unknown crystalline compound. X-ray diffraction data on this crystalline phase are given in Table 1.

Table 1 X-ray diffraction data

d	I/I_o	d	I/I_o	d	I/I_o
6.320	38.6	2.330	53.8	1.676	46.0
4.073	84.6	1.943	77.0	1.619	100
4.054	84.6	1.826	30.7	1.478	38.6
3.720	100	1.760	30.7	1.250	46.0
2.540	61.5	1.754	23.1		
2.520	61.5	1.702	53.8		

At 600°C, the mixture also contains GaN and Li_2O. In the temperature range 700–900°C, three consecutive endothermic effects are observed: a weak one at 720 and strong ones at 780 and 850°C. Up to 800°C, the mixture contains a new crystalline phase, GaN and Li_2O. At 850°C, this new compound decomposes, and Li_3GaN_2 and Li_5GaO_4 are formed (both identified by X-ray analysis). At this temperature, a slow loss in mass begins, and at 1200°C, it reaches a level corresponding to the evolution of all nitrogen from the reaction mixture. X-ray analysis shows the presence of Li_5GaO_4 and free gallium.

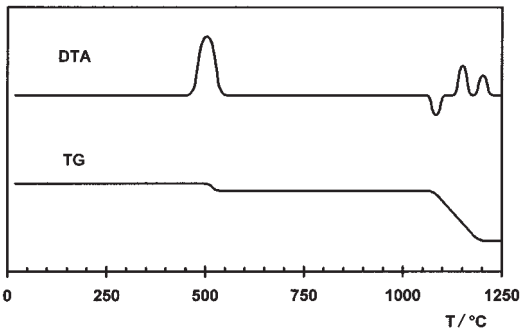

Fig. 3 TG and DTA curves of a mixture of Li_3N with $LiGaO_2$ (molar ratio 1:1), m=0.158 g, β=4°C min^{-1} (N_2)

The TG and DTA curves of a mixture of Li_3N with $LiGaO_2$ (molar ratio 1:1) are presented in Fig. 3.

The reaction starts with a strong exothermic effect at 500°C and an associated small loss in mass. X-ray diffraction analysis of the mixture obtained in a tube furnace at 500°C reveals formation of the crystalline phase obtained in the earlier experiment as a product of the reaction of Li_3N with Ga_2O_3 (X-ray diffraction data are given in Table 1).

The mixture also contains residues of unreacted Li_3N and $LiGaO_2$. At 700°C, only the presence of the new crystalline compound is observed. At 850°C, the new phase decomposes, with the formation of Li_5GaO_4 and Li_3GaN_2 (both identified by X-ray diffraction). In the temperature range 1000–1200°C, three thermal effects are observed, an endo one at 1080 and exo ones at 1150 and 1200°C. The loss in mass attains 9.52% at 1200°C, corresponding practically to complete elimination of nitrogen from the system. Elemental analysis demonstrates that the new compound obtained in the reaction of Li_3N with $LiGaO_2$ at 700°C has the stoichiometry Li_4GaNO_2 [9].

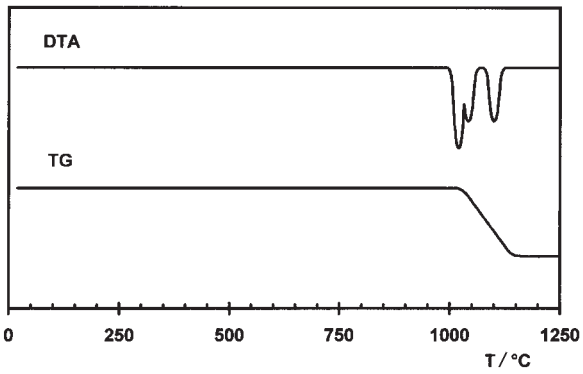

Fig. 4 TG and DTA curves of a mixture of GaN with Li_2O (molar ratio 1:2), m=0.143 g, β=4°C min^{-1} (N_2)

Figure 4 presents the TG and DTA curves of a 1:2 molar mixture of GaN with Li_2O under a nitrogen atmosphere.

At 1020, 1040 and 1100°C, endothermic effects are observed. The loss in mass starts at 1020, and at 1150°C it reaches 8.3% (the total content of nitrogen in the sample is 12.1%). Up to 1050°C, only the presence of the reactants (Li_2O and GaN) was confirmed by X-ray diffraction. X-ray examination of the products of reaction at 1050°C indicates the existence of Li_5GaO_4 and GaN (no Li_2O remains in the sample). At 1100°C, the presence of Li_5GaO_4 and free gallium is observed.

Analysis of the results leads to the following conclusions:

– The reaction of Li_3N with $LiGaO_2$ (molar ratio 1:1) at 700°C gives a new crystalline compound with the stoichiometry Li_4GaNO_2:

$$Li_3N+LiGaO_2 \rightarrow Li_4GaNO_2 \quad (1)$$

– The same crystalline phase is obtained in the reaction of Li_3N with Ga_2O_3 (molar ratio 2:1) at 600°C:

$$Ga_2O_3+2Li_3N \rightarrow Li_4GaNO_2+(Li_2GaNO) \rightarrow Li_2O+GaN \quad (2)$$

– The reaction of GaN with Li_2O starts at 1050°C. At this temperature, Li_4GaNO_2 is unstable.

– The thermal decomposition of Li_4GaNO_2 at 850°C produces two salts, both with pure coordination shells (pure oxide and pure nitride, respectively):

$$2Li_4GaNO_2 \rightarrow Li_5GaO_4+Li_3GaN_2 \quad (3)$$

At 900°C, Li_3GaN_2 decomposes as follows:

$$Li_3GaN_2 \rightarrow GaN+Li_3N\uparrow \quad (4)$$

The numbers of the above reactions correspond to the numbers of the transformations presented in the classification table (Fig. 1).

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