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FORMATION AND THERMAL DECOMPOSITION OF GERMANIUM NITROXY COMPOUNDS

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The formation of a previously unknown compound with the stoichiometry Li_3GeNO_2 was found during studies on the reactions of germanium dioxide with lithium nitride and of germanium oxynitride with lithium oxide.

Earlier studies on silicon oxynitride compounds led to the preparation of lithium and sodium salts containing $SiNO_2^{3-}$ [1, 2], $SiNO_3^{5-}$ [3] and $SiN_2O_2^{6-}$ [4] anions. The existence of other salts involving an oxynitride coordination shell round germanium was predicted on the basis of the morphological classification of simple species [1] and the analogy existing between known silicon and germanium compounds. Classification tables of known oxide, nitride and oxynitride species and of hypothetical germanium species (in parentheses) are presented in Figs 1 and 2. The axes describe the $e_z(O^{2-})$ and $e_z(N^{3-})$ parameters denoting the number of elementary negative charges formally introduced into the coordination shell by oxide or nitride ligands [1–5]. The routes of obtaining the previously hypothetical germanium salt Li_3GeNO_2 have been proposed on the basis of earlier studies on silicon oxynitrides [1–4]·

$$GeO_2 + Li_3N \rightarrow Li_3GeNO_2 \quad (1)$$

$$Ge_2N_2O + 3\,Li_2O \rightarrow 2\,Li_3GeNO_2 \quad (2)$$

(the numbering of reactions corresponds to the numbering of the transformations in Fig. 2). The compound formed during thermal decomposition should undergo transformation to two salts: a pure oxide and a pure nitride, as took place in the case of aluminium [5] and silicon [1–4] oxynitride salts, and in the thermal decompositions of cyanates.

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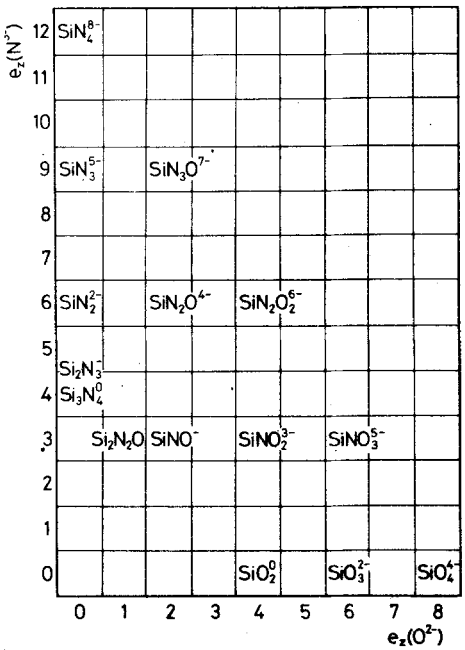

Fig. 1 Classification table of silicon oxynitride compounds

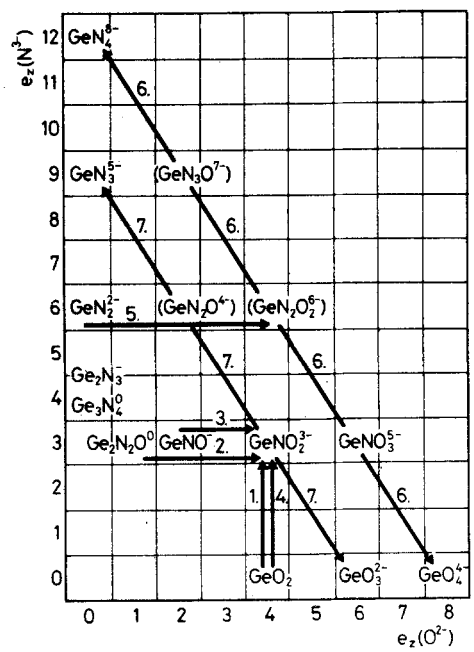

Fig. 2 Classification table of germanium oxynitride compounds

Apparatus and materials

The following compounds were used in the studies: GeO_2 (Koch Light Lab.), Li_3N (prepared in our laboratory), Ge_2N_2O (prepared in our laboratory), and Li_2O (Organic/Inorg. Research Lab.).

Initial examinations of the reaction course were carried out by thermal analysis methods on a MOM (Budapest) derivatograph. The synthesis of the new compound and its thermal decomposition were carried out in a tube furnace under an inert atmosphere. The products obtained in consecutive processes were studied by means of X-ray and classical analysis.

Results

The thermal curves of the GeO_2 and Li_3N mixture (1 : 1 mole ratio) are presented in Fig. 3. A strong exothermic effect occurs at 500°, connected with a small mass loss. At 680°, an endothermic effect is observed. Phase X-ray analysis shows the presence of a crystalline reaction product from 700°, this not being any of the known compounds of the Li–Ge–N–O system. The X-ray identification data relating to this phase are presented in Table 1. This species undergoes thermal

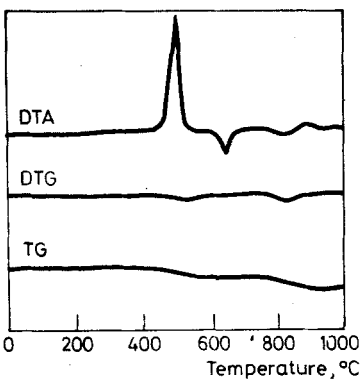

Fig. 3 TG, DTG and DTA curves of $GeO_2 + Li_3N$ in N_2 atmosphere. $m = 0.380$ g

Table 1 X-ray identification data on Li_3GeNO_2

d, Å	4.37	3.52	2.644	2.309	1.873	1.811	1.535	1.324
I/I_0	20	40	100	30	15	20	50	40

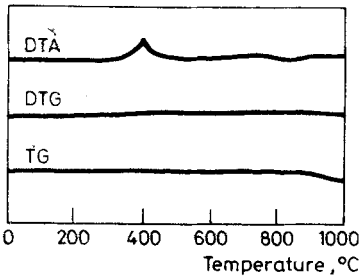

Fig. 4 TG, DTG and DTA curves of $Ge_2N_2O+3Li_2O$ in N_2 atmosphere. $m=0.278$ g

decomposition at 1200° to Li_2GeO_3 and Li_5GeN_3 (both these compounds were identified by the X-ray method).

The thermal curves of the Ge_2N_2O and Li_2O mixture (1 : 3 mole ratio) are presented in Fig. 4. A weak exothermic effect occurs at 400°, and the same crystalline phase as in the reaction of Li_3N and GeO_2 is formed from 600°. X-ray identification data concerning this phase are presented in Table 1.

The thermal decomposition at 1200° leads in this case too to Li_2GeO_3 and Li_5GeN_3.

Conclusions

Analysis of the results leads to the conclusion that the salt Li_3GeNO_2 is the obtained crystalline phase, formed as expected:

$$GeO_2 + Li_3N \rightarrow Li_3GeNO_2 \tag{1}$$

$$GeO_2 + N^{3-} \rightarrow GeNO_2^{3-}$$

$$Ge_2N_2O + 3\,Li_2O \rightarrow 2\,Li_3GeNO_2 \tag{2}$$

$$Ge_2N_2O + 3\,O^{2-} \rightarrow 2\,GeNO_2^{3-}$$

The thermal decomposition also proceeds according to the proposed schemes, with the formation of a pure oxide or pure nitride salt:

$$3\,Li_3GeNO_2 \rightarrow 2\,Li_2GeO_3 + Li_5GeN_3 \tag{3}$$

$$3\,GeNO_2^{3-} \rightarrow 2\,GeO_3^{2-} + GeN_3^{5-}$$

The preparation of other, at present hypothetical germanium oxynitride species indicated in the morphological table seems possible.

References

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Zusammenfassung — Während Untersuchungen über die Reaktionsfähigkeit von Germaniumdioxid und Germaniumoxynitrid gegenüber Lithiumoxid wurde die Bildung einer bis dahin unbekannten Verbindung der stöchiometrischen Zusammensetzung Li_3GeNO_2 festgestellt.

Резюме — При изучении реакции двуокиси германия или оксинитрида германия с окисью лития, обнаружено образование неизвестного ранее соединения стехиометрического состава Li_3GeNO_2.