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FORMATION AND THERMAL DECOMPOSITION OF SILICON OXYNITRIDE COMPOUNDS I

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The existence of formerly unknown compounds of the type $M^{I}_{3}SiNO_2$, suggested in previous papers, has been confirmed in reactions of lithium and sodium oxides with silicon oxynitride, Si_2N_2O.

In our studies on silicon oxynitride salts, special consideration has been given to silicon oxynitride, Si_2N_2O. In a recent paper we suggested the existence of a salt $Li(Na)_3SiNO_2$, formed in the reaction of silicon nitride with a corresponding oxide or of silicon dioxide with lithium nitride [1]. Figure 1 shows a classification table in the system of axes $e_zN^{3-} - e_zO^{2-}$, which represents the known silicon oxy compounds, silicon compounds with a nitride coordination shell, and compounds with mixed oxynitride coordination shells [2, 3]. The e_zO^{2-} number is the number

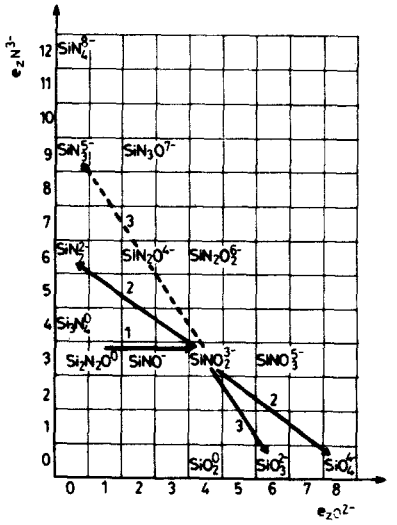

Fig. 1 Classificational table of oxynitride compounds of silicon

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of elementary negative charges formally introduced into the coordination shell by oxide ligands and e_zN^{3-} is the number of elementary negative charges formally introduced into the coordination shell by nitride ligands. Purely nitride anions of silicon lie on the $e_zO^{2-} = 0$ line and species with a purely oxide coordination shell lie on the $e_zN^{3-} = 0$ line. For example:

$$Si_3N_4: e_zO^{2-} = 0;\ e_zN^{3-} = 4 = \frac{4 \times 3}{3}$$

$$SiO_2: e_zO^{2-} = 4 = \frac{2 \times 2}{1};\ e_zN^{3-} = 0$$

$$Si_2N_2O: e_zO^{2-} = 1 = \frac{1 \times 2}{2};\ e_zN^{3-} = 3 = \frac{2 \times 3}{2}$$

$$SiNO^-: e_zO^{2-} = 2;\ e_zN^{3-} = 3$$

The addition of an oxide ligand causes an increase in the e_zO^{2-} number, and that of a nitride anione causes a corresponding increase in the e_zN^{3-} number.

Formal possibilities of using the morphological classification for the classification of heteroligand species have been presented in papers dealing with the fundamentals of the morphological classification of simple species [4–7]. During investigation of these compounds, it appeared more interesting to study the reactions leading to the formation of single compounds, such as the reaction $Li_3N + SiO_2$, while the reaction $Si_3N_4 + Li_2O(Na_2O)$ gives a mixture of at least two oxynitride salts [1]. Si_2N_2O seemed to be a good reagent, which was expected to yield single products in reactions with oxides.

Apparatus and reagents

The following substances were used in the work:

— silicon oxynitride, Si_2N_2O, synthesized in our laboratory,

— lithium oxide, Li_2O, produced by Research Organic and Inorganic Laboratories (USA),

— sodium oxide, Na_2O, produced by Fluka AG (FRG).

The courses of reactions were studied by thermal analysis with a derivatograph. The new compounds were synthesized in tube furnaces, using nickel boats and appropriate gas atmospheres. After freezing, the reaction products were studied by X-ray phase analysis, infrared absorption and classical analysis.

Results

Figure 2 presents the curve for a mixture of reagents corresponding to 3 $Li_2O + Si_2N_2O$. At 640° a weak exothermic effect with no loss of mass is observed. X-ray diffraction studies showed the presence of the phase Li_3SiNO_2, identified in former works as a product of the reactions $Li_3N + SiO_2$ and $Si_3N_4 + 6\ Li_2O$ [1].

$$Si_2N_2O + 3\ Li_2O \rightarrow 2\ Li_3SiNO_2 \qquad (1 \text{ in Fig. 1})$$

$$3\ O^{2-} + Si_2N_2O \rightarrow 2\ SiNO_2^{3-}$$

X-ray diffraction data for identification of this phase are given in Table 1.

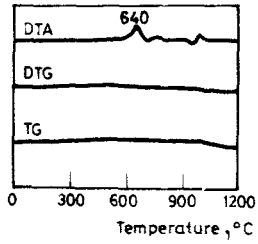

Fig. 2 Thermal curve of a mixture of $3Li_2O + Si_2N_2O$; m = 0.197 g

Table 1 X-ray diffraction data for identification of Li_3SiNO_2

d, Å	4.67	3.56	3.45	3.27	3.00	2.96	2.35	2.33	2.12	1.845
I/I_0	50	40	100	10	40	5	20	20	10	25

Infrared absorption studies have shown that the spectrum of the obtained phase is identical with those of the reaction products of $Li_3N + SiO_2$ and $Si_3N_4 + 6\ Li_2O$ [1]. Decomposition of the lithium oxynitride compound leads to the formation of Li_4SiO_4 and Li_2SiN_2 at 1250°:

$$2\ Li_3SiNO_2 \rightarrow Li_4SiO_4 + Li_2SiN_2 \qquad (2 \text{ in Fig. 1})$$

The products of this reaction were identified by X-ray phase analysis. The process is an acid-base disproportionation reaction in which the compound with a mixed oxynitride coordination shell on the silicon is decomposed to two compounds of higher thermal stability with uniform coordination shells [2, 3].

The reaction of sodium oxide with silicon oxynitride was also investigated.

A curve of a mixture of 3 $Na_2O + Si_2N_2O$ is given in Fig. 3. At 300° there is a strong exothermic effect with no loss in mass, connected with the formation of a new crystalline phase. Its X-ray diffraction pattern is identical with that of the reaction

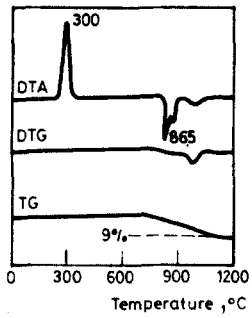

Fig. 3 Thermal curve of a mixture of $3Na_2O+Si_2N_2O$; $m = 0.176$ g

product of $Si_3N_4+6\ Na_2O$, determined in our former work as the salt Na_3SiNO_2 [1].

$$3\ Na_2O+Si_2N_2O \rightarrow 2\ Na_3SiNO_2$$

$$3\ O^{2-}+Si_2N_2O \rightarrow 2\ SiNO_2^{3-} \qquad \text{(1 in Fig. 1)}$$

Table 2 X-ray diffraction data for identification of Na_3SiNO_2

d, Å	4.85	3.85	3.65	3.48	2.66	2.63	2.32	2.28	2.17	2.12
I/I_0	40	40	10	30	20	60	100	80	60	10

The infrared spectrum is also identical with that presented in our previous work [1].

The obtained salt, Na_3SiNO_2, is stable up to 800°, at which it decomposes with the formation of Na_2SiO_3 and a small loss in mass. Attempts to identify the other products of decomposition failed because of their amorphous form. Classificational reasoning suggests that the other product should be a purely nitrogen compound, but its existence has not yet been confirmed [1].

$$3\ Na_3SiNO_2 \rightarrow 2\ Na_2SiO_3+Na_5SiN_3$$

$$3\ SiNO_2^{3-} \rightarrow 2\ SiO_3^{2-}+SiN_3^{5-} \qquad \text{(3 in Fig. 1)}$$

Conclusions

The reactions of silicon oxynitride with lithium and sodium oxides were investigated. The identified crystalline products, which are identical with the products of reactions of silicon nitride with the oxides and of silicon dioxide with

lithium nitride, are new evidence of the existence of the salts $M^I_3SiNO_2$. As the lithium salt Li_3SiNO_2 was obtained for the first time in the pure state, it became possible to determine the mechanism of its thermal decomposition, which follows the formerly established scheme and leads to products with a uniform coordination shell on the silicon atom [1, 2] (reaction path 2 in Fig. 1).

Silicon oxynitride should be useful for the synthesis of salts of the type $M^I_5SiNO_3$, which will be the subject of our subsequent studies.

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Zusammenfassung — Es wird gezeigt, daß in früheren Veröffentlichungen vermutete, bisher jedoch unbekannte Verbindungen des Typs $M^I_3SiNO_2$ bei Reaktionen von Lithium- und Natriumoxid mit Siliciumoxynitrid (Si_2N_2O) auftreten.

Резюме — Существование ранее неизвестных соединений типа $M^I_3SiNO_2$, предположенных в предыдущих статьях, было подтверждено реакцией окислов лития и натрия с оксинитридом кремния Si_2N_2O.