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FORMATION AND THERMAL DECOMPOSITION OF SILICON OXYNITRIDE COMPOUNDS. PART III

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The formation of a previously unknown compound with stoichiometry $Li_6SiN_2O_2$ was found during studies on the reactivity of Li_2SiN_2 with Li_2O, of SiO_2 with Li_3N and of Li_3SiNO_2 with Li_3N.

Earlier studies on the chemistry of silicon oxynitride salts led to the preparation of lithium and sodium salts containing $SiNO_2^{3-}$ [1. 2] and $SiNO_3^{5-}$ [3] anions. The existence of other salts involving a mixed oxynitride coordination shell round silicon was predicted on the basis of the morphological classification of the simple species [4]. The results presented here confirm the existence of a lithium salt with the $SiN_2O_2^{6-}$ anion.

Materials and apparatus

The following compounds were used in our studied:

Li_2SiN_2 — prepared in our laboratory;
Li_3SiNO_2 — prepared in our laboratory;
Li_3N — prepared in our laboratory;
Li_2O — p.a. product of POCh–Poland.

Initial studies 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 under an inert atmosphere in a tube furnace. The products obtained in consecutive processes were studied by means of X-ray and classical analyses.

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Results

From the reaction of a mixed silicon-lithium nitride, Li_2SiN_2, with Li_2O at 900°, a crystalline phase is obtained which is not identical with any of the known compounds that may be formed from those reactants. TG, DTG and DTA curves of the mixture of reactants Li_2SiN_2 and Li_2O in a 1 : 2 molar ratio are given in Fig. 1. The exothermic effects at 560° and 840° may indicate the synthesis of the compound of interest. X-ray data on the phase obtained are given in the table below:

d Å	5.01	4.21	3.01	2.897	2.536	1.926
I/I_0	100	25	30	35	90	90

Li_3SiNO_2 is the second crystalline product, formed in parallel at 900°.

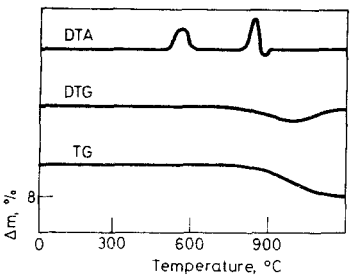

Fig. 1 TG, DTG and DTA curves of $Li_2SiN_2 + 2\ Li_2O$; m = 0.239 g, N_2

The presence of Li_5SiN_3 and Li_4SiO_4 was found in the thermal decomposition products of such a mixture at 1100°, i.e. compounds with a purely nitride coordination shell or a purely oxide coordination shell round the central silicon.

Such a decomposition route is in agreement with our earlier predictions [4].

The course of the reaction between SiO_2 and Li_3N is also interesting. TG, DTG and DTA curves of the SiO_2 and Li_3N mixture at a 1 : 2 molar ratio are presented in Fig. 2.

The exothermic effect at 560° indicates that the following reaction proceeds [1, 2]:

$$SiO_2 + Li_3N \rightarrow Li_3SiNO_2$$

X-ray analysis indicates the presence of Li_3N and Li_3SiNO_2. Only after fusion (endothermic effect at 845°) does Li_3N react further:

$$Li_3SiNO_2 + Li_3N \rightarrow Li_6SiN_2O_2$$

X-ray analysis indicates the presence at 900° of a crystalline product with identical

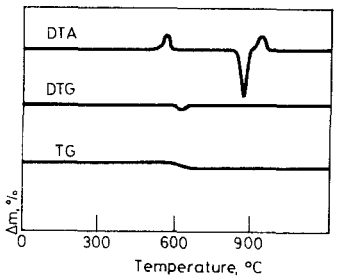

Fig. 2 TG, DTG and DTA curves of $SiO_2 + 2\ Li_3N$; $m = 0.380$ g, N_2

identification data to those of the product obtained from the reaction of Li_2SiN_2 with Li_2O. The thermal decomposition of the new phase at 1100° leads to Li_4SiO_4 and compounds containing nitrogen that are amorphous.

The reaction of Li_3SiNO_2 as initial substrate with Li_3N leads to similar products: first to a new crystalline phase, and then to Li_4SiO_4 and Li_8SiN_4 resulting from the thermal decomposition. The thermal decomposition products were identified in this case by X-ray methods.

Conclusions

The reactions of Li_2SiN_2 with Li_2O, and of SiO_2 or Li_3SiNO_2 with Li_3N have been studied. In all three processes the reaction product is the same, previously unknown crystalline phase.

The oxide, nitride and the previously obtained oxynitride silicon salts are presented in the classification table in Fig. 3. The axes are described by $e_z(O^{2-})$ and $e_z(N^{3+})$ numbers, which express the number of elementary negative charges formally introduced into the coordination shell by oxide or nitride ligands. An analysis of the possible course of consecutive reactions leads to the conclusion that the crystalline phase is $Li_6SiN_2O_2$, formed in the following transformations:

$$\begin{aligned} Li_2SiN_2 + 2\ Li_2O &\rightarrow Li_6SiN_2O_2 \\ SiN_2^{2-} + 2\ O^{2-} &\rightarrow SiN_2O_2^{6-} \end{aligned} \quad (1)$$

$$\begin{aligned} SiO_2 + 2\ Li_3N &\rightarrow Li_6SiN_2O_2 \\ SiO_2 + 2\ N^{3-} &\rightarrow SiN_2O_2^{6-} \end{aligned} \quad (2)$$

$$\begin{aligned} Li_3SiNO_2 + Li_3N &\rightarrow Li_6SiN_2O_2 \\ SiNO_2^{3-} + N^{3-} &\rightarrow SiN_2O_2^{6-} \end{aligned} \quad (3)$$

The directions of transformations under the influence of anionizing reagents cross at the site corresponding to $SiN_2O_2^{6-}$ (the numbers of the reactions

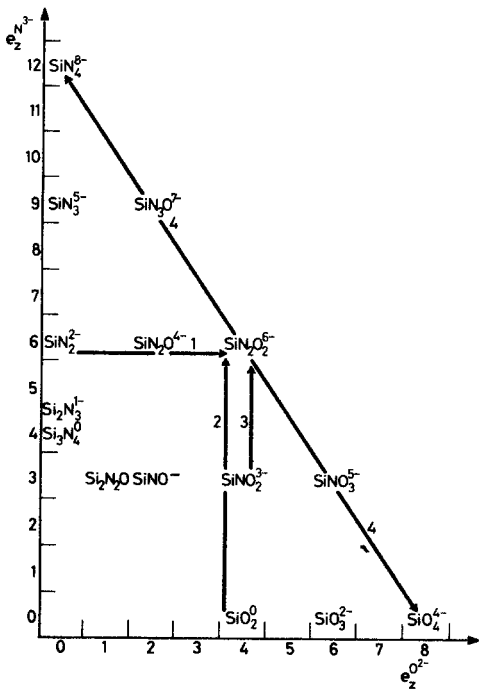

Fig. 3 Classification table of silicon oxynitride compounds

correspond to the numbers of the transformations indicated in the classification table).

The course of thermal decomposition of the new salt is in agreement with that predicted [2, 3, 4] and proceeds to purely oxide and purely nitride salts:

$$2\ Li_6SiN_2O_2 \rightarrow Li_8SiN_4 + Li_4SiO_4 \qquad (4)$$
$$2\ SiN_2O_2^{6-} \rightarrow SiN_4^{8-} + SiO_4^{4-}$$

It appears possible to obtain further hypothetical species shown in the classification table (SiN_3O^{7-} and SiN_2O^{4-}) from the reactions of salts containing SiN_3^{5-} and SiN_2^{2-} anions with lithium oxide and of $SiNO^-$ with nitride.

References

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Zusammenfassung — Die Bildung einer bisher unbekannten Verbindung der Stöchiometrie $Li_6SiN_2O_2$ wurde bei Untersuchungen der Reaktivität von Li_2SiN_2 mit LiO, von SiO_2 mit Li_3N und von Li_3SiNO_2 mit Li_3N beobachtet.

Резюме — Образование нового соединения состава $Li_6SiN_2O_2$ установлено при изучении реакций Li_2SiN_2 с окисью лития, двуокиси кремния с нитридом лития, а также при взаимодействии Li_3SiNO_2 с нитридом лития.