

PREPARATION AND ELECTROCHEMICAL PROPERTIES OF DOUBLE-METAL NITRIDES CONTAINING LITHIUM

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Summary

A study is reported of the preparation, chemical composition, and crystal structure of binary compounds of Li_3N with other nitrides, *i.e.*, Mg_3N_2 , AlN , BN , and Si_3N_4 . Most of the crystal structures are related to an antifluorite system. Except for LiMgN , the compounds are pure lithium ion conductors. A new compound, Li_8SiN_4 , has the highest lithium ion conductivity (*viz.*, $1 \times 10^{-3} \text{ S m}^{-1}$ at 298 K) of the double-metal nitrides investigated.

Introduction

In order to develop solid lithium batteries, it is necessary to find new lithium ion conductors that have higher conductivity and better stability than materials examined to date [1, 2]. ZrO_2 and $\beta\text{-PbF}_2$ with fluorite-type crystal structures are well-known conductors of anions. An antifluorite-type structure, where the roles of cation and anion are opposite to those in the fluorite structure, could prove suitable for cationic conduction. Juza *et al.* [3] have prepared double-metal nitrides containing lithium, represented as $\text{Li}_{2x-3}\text{M}^x\text{N}_{x-1}$ where M is a metalloid such as Mg, Zn, Al, Ga or Ti. These nitrides have crystal structures related to antifluorite, but there has been no systematic investigation of their ionic-conduction properties.

In a high-pressure study of Li_3BN_2 , DeVries and Fleisher [4] assumed that the normal pressure phase had an antifluorite derivative structure because both boron and aluminium were IIIb elements. The high-temperature crystal structure has been determined recently [5, 6]. Juza *et al.* [7] prepared Li_5SiN_3 having an antifluorite superstructure. Lang and Charlot [8] also examined the possible presence of other compounds in the Li_3N - Si_3N_4 system. These authors succeeded in synthesizing three new phases: LiSi_2N_3 , Li_2SiN_2 , and Li_8SiN_4 , but were unable to obtain the Li_5SiN_3

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reported by Juza *et al.* [7]. However, many ambiguities still remain in the $\text{Li}_3\text{N}-\text{Si}_3\text{N}_4$ system.

This work discusses recent studies of the preparation, chemical composition, and crystal structure of double-metal nitrides containing lithium [5, 6, 9, 10]. The conductivities of these compounds for lithium ions are also reported.

Experimental

Lithium nitride (Li_3N) was prepared by the reaction of nitrogen gas (Osaka Oxygen Ind. Ltd., 99.999%) with lithium metal (Wako Pure Chemical Ind. Ltd., 99%) within a temperature range of 375 K - 475 K. The lithium nitride was separately mixed with the following nitrides: AlN (Rare Metallic Co. Ltd., 99.8%), BN (Showa Denko Co., 99.8%), Si_3N_4 (Ube Industries, 98%), and Mg_3N_2 which was prepared by the reaction of granular magnesium (Mitsuwa Pure Chemicals, 99%) with nitrogen gas at 1175 K. These mixtures were pressed into pellets and heated at 975 K - 1275 K under a nitrogen atmosphere. The products were characterized by X-ray powder diffraction (XRD). The complex impedance was measured in the range 5 Hz - 10 MHz using a multifrequency LCR meter (YHP 4275A) and a vector impedance meter (HP 4800). Both sides of each sample disc were coated with conductive silver paste or carbon. The electronic contribution was estimated by the d.c. method using carbon or molybdenum as ion-blocking electrodes. Crystal structures of Li_3BN_2 were examined for single crystals of both the α -phase ($0.15 \times 0.1 \times 0.1$ mm) and the β -phase ($0.8 \times 0.5 \times 0.5$ mm), using a four-circle diffractometer (Rigaku AFC-5 FOS).

Results and discussion

Li₃N-AlN system

Single-phase Li_3AlN_2 was prepared by heating mixtures of $\text{Li}_3\text{N}/\text{AlN}$ in a 1.2 - 1.5 molar ratio on an AlN disc at 875 K and 1175 K [9]. Excess Li_3N was evaporated during the heat treatment. Li_3AlN_2 has an antifluorite superstructure (cubic, $a = 9.470$ Å). Figure 1 shows the temperature dependence of the ionic conductivity of Li_3AlN_2 . The conductivity and activation energy were 5×10^{-6} S m^{-1} at 298 K and 52 kJ mol^{-1} , respectively. An $\text{Li}/\text{Li}_3\text{AlN}_2/\text{TiS}_2$ cell gave an open-circuit voltage (OCV) of 2.5 V. This value was similar to that observed on Li/TiS_2 cells using a liquid organic-solvent electrolyte [11].

Li₃N-BN system

The low (α) and high (β) temperature phases of Li_3BN_2 were prepared from mixtures of $\text{Li}_3\text{N}/\text{BN}$ in a 1.0 - 1.1 molar ratio. The mixture was pressed into pellets, wrapped in tantalum foil, and then heated at a tempera-

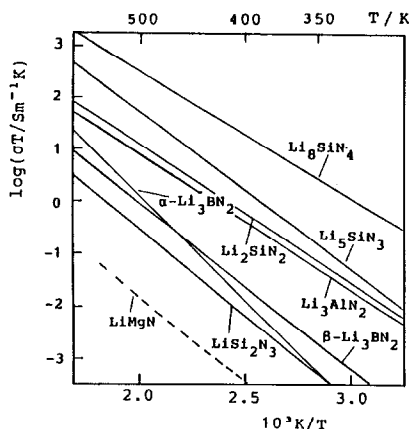


Fig. 1. Ionic conductivities of double-metal nitrides containing lithium.

ture ranging from 1070 K to 1170 K under a stream of nitrogen. The β -phase is a new polymorph of lithium boron nitride. The phase transition temperature and the melting point of this phase are around 1135 K and 1189 K, respectively. The α - Li_3BN_2 compound has tetragonal symmetry, $P4_22_12$, with $a = 4.6435(2)$ Å, $c = 5.2592(5)$ Å, $Z = 2$, $D_{\text{calc.}} = 1.747$ mg m $^{-3}$, and $R = 0.042$. On the other hand, β - Li_3BN_2 has monoclinic symmetry, $P4_22_12$, with $a = 4.6435(2)$ Å, $c = 5.2592(5)$ Å, $Z = 2$, $D_{\text{calc.}} = 1.737$ mg m $^{-3}$, $R = 0.023$. The low-temperature phase (α) has a slightly higher density than the high-temperature phase (β).

The crystal structures of these phases are shown in Fig. 2. Each contains a linear $(\text{NBN})^{3-}$ anion group that is isoelectronic with $(\text{NNN})^-$ in azide and $(\text{NCN})^{2-}$ in cyanamide.

The α - Li_3BN_2 structure is related to an antifluorite structure where the anions comprise a face-centred lattice and the cations are located in the tetrahedra of the anions. The arrangement of nitrogen atoms in α - Li_3BN_2 can

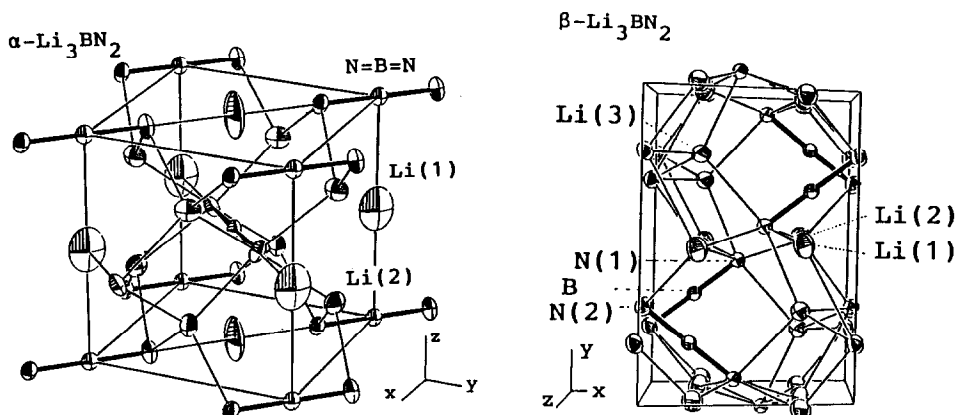


Fig. 2. Crystal structures of α - and β - Li_3BN_2 .

be recognized as a face-centred lattice, in which the central nitrogen is a little off-centre due to the presence of the NBN group [6]. Boron and Li (1) in α - Li_3BN_2 are co-ordinated with two nitrogen atoms and are on the edge of nitrogen tetrahedra. Li (2) is located in the nitrogen tetrahedra, as in the antifluorite structure.

In β - Li_3BN_2 , all the lithium ions are tetrahedrally surrounded by nitrogen atoms. The tetrahedra are distorted. The arrangement of nitrogen is not directly related to a face-centred lattice, as in the case of β - Li_3BN_2 .

The lithium ion conductivities were 3×10^{-5} and 6×10^{-5} S m^{-1} at 400 K for the polycrystalline samples of α - and β - Li_3BN_2 , respectively. The activation energy of β - Li_3BN_2 (64 kJ mol^{-1}) was smaller than that of α - Li_3BN_2 (78 kJ mol^{-1}). This difference can be partly explained in terms of structural considerations. The crystal structure of the high-temperature phase, β - Li_3BN_2 , is more distorted and less rigid than that of the low-temperature phase, α - Li_3BN_2 .

Li₃N-Si₃N₄ system

Single-phase Li_8SiN_4 was prepared by heating a mixture of $\text{Li}_3\text{N}/\text{Si}_3\text{N}_4$ in an 8.2 molar ratio at 1075 K. The XRD pattern did not coincide with any other data previously reported for this system [7, 8]. The crystalline phase exhibited a tetragonal symmetry with $a = 10.217 \text{ \AA}$ and $c = 9.536 \text{ \AA}$. The unit cell can be represented as a superlattice of antifluorite [10]. Lang and Charlot [8] have reported the presence of Li_8SiN_4 with an XRD pattern that fits the data for $\text{Li}_{18}\text{Si}_3\text{N}_{10}$ prepared here. The chemical compositions of the present products were confirmed by chemical analysis.

Li_5SiN_3 was prepared from a mixture of $\text{Li}_3\text{N}/\text{Si}_3\text{N}_4$ in a 5.1 molar ratio at 1075 K. The compound has an antifluorite structure (cubic $a = 4.724 \text{ \AA}$). Both LiSi_2N_3 and Li_2SiN_2 have also been synthesized [8]. The crystal structure of LiSi_2N_3 was wurtzite-type [12], but that of Li_2SiN_2 is yet to be determined.

Figure 1 shows the ionic conductivities of LiSi_2N_3 , Li_2SiN_2 , Li_5SiN_3 and Li_8SiN_4 . Li_8SiN_4 has the highest conductivity ($1 \times 10^{-3} \text{ S m}^{-1}$ at 298 K) and the lowest activation energy (47 kJ mol^{-1}) of the series of compounds synthesized here.

Li₃N-Mg₃N₂ system

Single-phase LiMgN was prepared from an $\text{Li}_3\text{N}/\text{Mg}_3\text{N}_2$ mixture in a 1.2 molar ratio at 1275 K. LiMgN has an antifluorite structure (cubic, $a = 4.988 \text{ \AA}$), and the conductivity was the lowest of the compounds studied (Fig. 1). Direct-current measurements with carbon electrodes indicated that electron and/or hole migrations contribute to less than 80% of the total conduction. Lithium-ion migration could be obstructed by a statistical occupation of the cation sites by divalent magnesium ions [13].

Compounds with crystal structures related to antifluorite exhibited lithium-ion conduction in a series of double-metal nitrides containing lithium. Pure lithium-ion conduction was observed in the following products: Li_3AlN_2

and Li_5SiN_3 with antiferroite structure, and $\alpha\text{-Li}_3\text{BN}_2$ with a structure derived from an antiferroite structure. Ionic conduction was quite low in the case of LiMgN , where the lithium content in the unit formula was the least of the double-metal nitrides. Li_8SiN_4 , with the highest lithium content, showed the highest conductivity of the products in the present study. Lithium-ion conduction was also observed in $\beta\text{-Li}_3\text{BN}_2$, Li_2SiN_2 , and LiSi_2N_3 .

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