New anti-fluorite solid-solution phases in Li–Ti–N ternary system

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New Li–Ti–N solid-solution compounds with an anti-fluorite-type superstructure were synthesized by heating the mixture of Li₃N and TiN at 800°C in Ar flow. The compositions of the new compounds seem to lie on the tie-line between the two well-known compounds, Li₃N (hexagonal, P6₃/mmm) and Li₅TiN₃ (cubic, I2ₐ/a-3) by Li evaporation during heating in Ar gas flow, and nominally represented with LiₓTiₓNₓ. The solubility is large; the anti-fluorite-type superstructure of Li₅TiN₃ (y = 0) was retained up to y = ca. 0.9, which is close to the end member Li₅N (y = 1) with a different layered structure. This finding opens up further exploring other new Li–M–N (M = transition metals, group XII, or XIV elements) phases with some attractive functions.

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1. Introduction

Lithium nitride and lithium metal nitrides form a promising materials group for energy storage and conversions, such as anode for lithium secondary battery, lithium ion conductor, and hydrogen storage. For example, Li₃MnN₄ (200 mAh/g, 1.2 V vs. Li/Li⁺), Li₂FeN₂ (130 mAh/g, 1.2 V vs. Li/Li⁺), Li₂Fe₁₋ₓNₓ (550 mAh/g, 0.05–1.3 V vs. Li/Li⁺), Li₂Cr₁₋ₓNₓ₄ (700–900 mAh/g, 0.6 V vs. Li/Li⁺), Li₂⁺₃Nₓ₂ (400 mAh/g, 0.6 V vs. Li/Li⁺), Li₂⁺₃Cu₁₋ₓNₓ (400 mAh/g, 0.6 V vs. Li/Li⁺) were reported to show reversible lithium deintercalation and reintercalation. As lithium ion conductors, Li₃N itself shows high lithium conductivity of > 10⁻³ Scm⁻¹ at room temperature but its low decomposition voltage of 0.44 V vs. lithium has prohibited to be used for practical application. To combat this problem, ternary systems such as Li₃–ₓCaₓNₓ (x = 1–3), Li₅BN₃, LiₐAlNₐ, and Li–Si–N phases were thoroughly investigated. Recently, Chen et al. reported a large hydrogen storage capacity of 6.7 wt% upon Li₃N under 0.3 MPa of H₂ at 255–285°C by reversible deintercalation into lithium amide, LiNH₂, or lithium imide, Li₄NH.

As for Li–M–N ternary system, when M = 3d transition metals, the general acceptance is that the anti-fluorite (anti-CaF₂) structure with general chemical formula, Li₂₋ₓMₓNₓ, is stabilized when M is early transition metals, Sr–Fe, as Li₃TiN₃ (n = 3), Li₅VN₃ (n = 4), Li₅CrN₄ (n = 4, 5), Li₅CrₓN₄₋ₓ (n = 4), Li₅MnN₄ (n = 4), and Li₅FeN₂ (n = 2), where nitrogen atoms form cubic closed packed sub-array (Ca site in fluorite CaF₂) and all of the tetrahedral sites (F sites in fluorite CaF₂) are occupied by lithium or transition metal atoms with regular arrangements. While, Li₅N-type structure is the ground state forming solid solutions as LiₓMₓNₓ when M is late transition metals, Co, Ni, and Cu. Lithium nitride has a layered structure belonging to the space group P6₃/mmm with two different lithium sites, Li(1) and Li(2). The Li₃N layer is formed by Li(2) in ab plain with edge-shared NLi₆ hexagons and Li(1) positions between layers to form continuous Li(1)–N–Li(1) chain along c-axis. Although such an overall classification shown in Fig. 1 has been well established, detailed phase relationship depending on the synthetic conditions and/or Li/M ratio has to our knowledge not been documented before.

In this paper, we took a closer look at the Li–Ti–N ternary system towards some new phases which may not be categorized into the above empirical general rule. Attention was focused on the effect of Li/Ti ratio in the starting precursor as well as of the atmospheric gas in the sintering processes. In the previous literature, anti-fluorite-type Li₅TiN₃ has been believed to be the only stable phase in the Li–Ti–N ternary system and synthesized by sintering Li₃N and TiN at 1040–1080°C under NH₃ or N₂ gas. The external nitrogen source is necessary because the line between Li₅N and TiN positions in the nitrogen-poor region in the ternary phase diagram as compared with the Li₅TiN₃ point (Fig. 2). Our principal concern at this stage was that some new phases may be obtained by sintering under inert atmosphere without nitrogen.
2. Experiments

Powders were synthesized via a solid-state reaction. All procedure, including sample transport, mixing, sintering, was performed in an inert atmosphere (dewpoint < -65°C). Lithium nitride Li₃N (High Purity Chemical Co., > 99.99%) and titanium nitride TiN (Wako Pure Chemical Ind., Ltd., > 98.7%) were used as starting materials; the molar ratio \( x \) in \( x \text{Li}_3\text{N}(100-x)\text{TiN} \) was varied from 65 to 97.5, as indicated in Fig. 2. A total of approximately 4 g were sealed into a 250-ml Cr-hardened SUS container together with a mixture of 10 mmφ × 5 and 5 mmφ × 30 Cr-hardened SUS balls. This was thoroughly mixed and reground by conventional planetary milling (Ito Co., LP–4) for 6 h at 240 rpm, followed by sintering at 700–800°C for 24 h in a pellet form under a Ar (99.9995%) or N₂ (99.9999%) gas flow with 50 cc/min. Heating and cooling rate was 8°C/min. Sintering was performed using molybdenum sample boat set in the SUS reactor tube.

X-ray diffraction patterns of the powdered samples were obtained with an X-ray diffractometer (Rigaku Co. RAD-C, 12 kW) with Cu Kα radiation. The diffraction data were collected at 0.02 step widths over a 2θ range from 10° to 100°. The chemical compositions of the final products were checked by atomic absorption spectrometer (Hitachi, Ltd., Z–2300).

X-ray absorption spectroscopy for Ti K-edge was performed using LOOPER 2000 (Rigaku Co.) with an energy step in 1 eV. The sample was firmly sealed into KAPTON film to avoid any contamination by reacting with air and/or moisture. Standard samples of TiO (Aldrich, 99.9%) and rutile TiO₂ (High Purity Chemicals Co., Ltd., 99.9%) were used.

3. Results and discussions

Powder X-ray diffraction profiles measured for samples obtained by sintering the mixture of various Li₃N:TiN molar ratios at 800°C are given in Fig. 3. Details on the identified phases are summarized in Fig. 4. Even at a first glance, the phases sintered under N₂ and Ar were entirely different. The color of samples prepared under N₂ was always dark brown or dark grey, while the color of samples prepared under Ar was always pale yellow.

The dark color is the signal of residual starting materials, Li₃N (dark reddish brown) or TiN (dark blue-green). This is also supported by the X-ray diffraction profiles themselves, where the samples sintered under N₂ was complicated and analyzed as a mixture of anti-fluorite derivatives, low-temperature stable phase Li₈TiN₄, Li₃N-related phase, and residual TiN. Apparently, the reaction in N₂ gas is incomplete at 800°C and is consistent with the previous report that much higher temperature of > 1000°C is necessary to synthesize the single phase of Li₅TiN₃ with an anti-fluorite-type superstructure even under NH₃ atomosphere.

On the other hand, the samples synthesized in the Ar flow showed a systematic change of X-ray diffraction (XRD) profile maintaining the anti-fluorite-type structure framework. For a wide range of starting molar ratio between \( x = 65 \) and \( x = 95 \), no parasite signal was observed and all diffraction peaks were indexed with a cubic lattice of the anti-fluorite-type structure framework. The major systematic changes as a function of \( x \) were found in the suppression in (211), (312) peaks, the simultaneous enhancement in (222) peak, and the monotonic decrease in the cubic lattice constant as shown in Fig. 5. Note that the lattice constant for the sample with starting molar ratio \( x = 65 \) is close to that of the well-known anti-fluorite-type Li₅TiN₃. It is also noteworthy that the anti-fluorite-type structure framework is...
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retained up to \( x = 95 \), which is close to the end member \( \text{Li}_3\text{N} \) with entirely a different layered structure.

Based on the preceding results, overall schematic diagram for final products along TiN–Li\(_3\)N binary line (65 < \( x < 100 \)) are given in Fig. 4. The emphasis is given to the differences when they are sintered in \( \text{N}_2 \) and \( \text{Ar} \) flow. Three major differences are i) for almost whole region of 65 < \( x < 100 \), continuous solid solution forms in \( \text{Ar} \), whereas multi-phase mixture is always the case in \( \text{N}_2 \), ii) the presence of residual starting materials, \( \text{Li}_3\text{N} \) and TiN, in \( \text{N}_2 \) by incomplete reaction, and iii) the presence of \( \text{Li}_5\text{TiN}_4 \) phase in \( \text{N}_2 \). The existence of \( \text{Li}_5\text{TiN}_4 \) phase (P4\( \bar{3} \)/nm) has just recently been reported\(^{21} \) and it can be synthesized only by the low-temperature (< 400°C) sintering in \( \text{N}_2 \) flow. Therefore, it is reasonable that any \( \text{Li}_5\text{TiN}_4 \) phase was not found in the sample sintered at relatively high temperature of 800°C in \( \text{Ar} \) flow.

Hereafter, we will focus on the new continuous solid solutions obtained by sintering at 800°C in \( \text{Ar} \) (Figs. 3(b) and 4(b)). First of all, X-ray absorption spectra of Ti K-edge measured for the sample from \( \text{Li}_3\text{N}:\text{TiN} = 75:25 \) mixture is shown in Fig. 6, together with those of standard samples, TiO and rutile \( \text{TiO}_2 \). It is reasonable that the absorption edge is at much higher energy than that of Ti\(^{2+}\)O and rather close to that of Ti\(^{4+}\)O\(_2\), as the color of the whole series of samples was pale yellow, which is as same as that of \( \text{Li}_5\text{Ti}^{4+}\text{N}_4 \). Note that the immediate electrochromic response to dark blue is general when there is even a slight reduction of Ti from tetravalent. The pre-edge feature A is due to the dipole forbidden 1s 3d transition, which has been known to become visible under the lower symmetry with significant shift in the peak position to lower energy.\(^{23,24} \) Indeed, negligible pre-edge feature was observed for Ti in the symmetric octahedral sites in TiO, while the pre-edge structure is clear for rutile \( \text{TiO}_2 \) where the TiO\(_6\) octahedra are strongly distorted. In the present new Li–Ti–N sample, the pre-edge peak is much more pronounced with a clear shift to the lower energy, and hence it is reasonable to speculate that Ti is located in the tetrahedral site in the original anti-fluorite structure. Contribution from the Ti migrated to the vacant octahedral sites is unlikely because of its highly symmetric environment.

Following these tracks, here we show the results of profile simulations by assuming that all Ti atoms are fixed in the tetrahedral site and are always tetravalent. Two possible structural models were considered; (a) titanium are substituted by the excess lithium with simultaneous formation of the nitrogen defect for charge neutrality, thereby the solid solution can be written as \( \text{Li}_5\text{Ti}^{4+}\text{N}_3\text{Li}^+\text{Ti}^{3+}\text{N}_4 \)\(_{16}\) and (b) the excess lithium occupy not only the original Ti 16c sites but also the vacant octahedral 24d sites, thereby the solid solution can be written as \( \text{Li}_5\text{Ti}^{4+}\text{N}_3\text{Li}^+\text{Ti}^{3+}\text{N}_4\text{Li}_y\text{Ti}_{1-y}\text{N}_4 \)\(_{24}\). Figure 7 summarizes the simulation results, which obviously show the model (a) gives more reasonable profiles close to the experimental results. Loss of lithium during the synthesis was estimated to be ca. 3 percent of the total lithium by atomic absorption spectroscopy, which might be responsible to adjust the final composition into the \( \text{Li}_3\text{N}–\text{Li}_5\text{TiN}_4 \) tie-line maintaining Ti in tetravalent state, as the \( \text{Li}_5\text{N}–\text{TiN} \) raw materials line (Ti in trivalent state) positions slightly lithium-rich side of the final product (see Fig. 2). Although it is likely that nitrogen defects function for

![Fig. 4. Schematic derivation of the final products by sintering TiN/LiN mixture in various ratios at 800°C under (a) \( \text{N}_2 \) flow and (b) \( \text{Ar} \) flow.](image)

![Fig. 5. Variation of the lattice constant for the new anti-fluorite phase obtained by sintering \( x\text{Li}_3\text{N}-(100-x)\text{TiN} \) mixtures at 800°C in \( \text{Ar} \) flow.](image)

![Fig. 6. Ti K-edge X-ray absorption near edge spectra of the new compound with anti-fluorite structure obtained by sintering the \( x\text{Li}_3\text{N}-(100-x)\text{TiN} \) mixture (\( x = 70 \)) in \( \text{Ar} \) flow.](image)
charge compensation with respect to the present preliminary analysis, more detailed investigations using neutron diffraction data would be necessary to determine the valid structure including the position and occupancy of light elements such as lithium and nitrogen.

4. Conclusion

The new lithium-rich compounds with anti-fluorite-type structure framework were synthesized in Li–Ti–N ternary system by sintering mixture of Li₃N and TiN with various ratios at 800°C under pure Ar flow. The definitive valid structure is not clear at the moment, but the preliminary analysis led to speculate the nitrogen defect model, [Li₅][Li_yTi₁–y][N₃–y]_{a,24d}.

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