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Structures of boron nitride intercalation compound with lithium synthesized by mechanical milling and heat treatment

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ABSTRACT

Hexagonal boron nitride (h-BN) exhibits a layered solid structure such as graphite, and the h-BN intercalation compounds (BNICs) have been actively studied as with graphite intercalation compounds (GICs). It is difficult, however, to synthesize BNICs compared with GICs, where the synthesis of BNICs requires high temperature and/or pressure. In this study, the Li-BNIC is synthesized by ball milling and heat treatment, and the samples were characterized by X-ray diffractomety (XRD), differential thermal analysis (DTA) and ^{7}Li NMR (nuclear magnetic resonance) study.

New XRD peaks corresponding to Li-BNICs were observed from the milled sample after heat treating at 700 °C for 2 h. The shifted peaks of h-BN to the lower angles imply an expanded BN lattice through Li insertion. The exothermic DTA peaks observed between 200 and 500 °C might be the synthesis temperatures of Li-BNIC. The NMR spectra of the Li-BNIC are modified according to the ratio of Li to BN, although the corresponding XRD patterns are not changed.

1. Introduction

Hexagonal boron nitride (h-BN) has been receiving lots of attention due to the lattice structure (a = 2.505 Å, c = 6.66 Å) [1] similar to graphite (a = 2.45 Å, c = 6.70 Å) [2], i.e. both exhibiting a characteristic layered structure. Through making good use of this property, various intercalation compounds have been synthesized by inserting atoms or molecules into the interlayers, which are still being discussed and researched. Especially, alkali-metal GICs (graphite intercalation compounds) have been actively studied due to their interesting properties including superconductivity and electrochemical intercalation of anodes for Li-ion batteries [3]. Also, in case of h-BN, intercalation of alkali metal [4–6], transition metal [7] or molecules (Br_2 [8], $S_2O_6F_2$ [9] and Brønsted acids [10]) has been reported, where the intercalation is more difficult compared with graphite because the interlayer interaction of h-BN is stronger than that of graphite. This is due to partial ionic characteristics of h-BN originating from the charge transfer from N to B.

Sakamoto et al. have reported intercalation of Cs and Br into h-BN [8], where Br does not intercalate into BN while there is a possibility of intercalation for Cs. In case of potassium intercalation reported by Doll et al., the K atoms occupy the (2 × 2) R (0°) superlattice, which is commensurate with the BN lattice [5]. Budak et al. also tried to attain intercalation of h-BN using transition metals (Cr, Mn, Fe, Co, Ni, Cu, Zn, and Ag) and reported a change in the interlayer spacing due to the intercalation of Cr, Mn, Fe and Ag according to X-ray diffractometry (XRD) [7]. Shen et al. reported synthesis of $(BN) \sim 3SO_3F$ that exhibits metallic electrical conductivity and an increase in interlayer distance [9], and Kovtyukhova et al. reported reversible intercalation of h-BN with Brønsted acids [10]. Sumiyoshi et al. also reported successful synthesis of Li-BNIC (BN intercalation compound) at 1250 °C for 10 h, where its interlayer distance was expanded by 12.86% [6].

These h-BN intercalation compounds (BNICs) were reported synthesized mainly under high temperatures and at high pressure such as hot press or using a two-zone vapor transport technique, which is one of the synthesis methods for GICs and other intercalations. However, no report has been issued on the mechanical milling (MM) process for producing BNICs, while Li-GICs are reported to be synthesized by ball milling [11–13].

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Mechanical milling (MM) is a technique of a solid-state powder processing and one of the processes to produce supersaturated solid solutions, nano-crystal alloys, non-equilibrium phase alloys and so on [14]. This process also enables to induce a reaction that would take place in a finely dispersed powder through welding and pulverizing in a solid state. It is thus expected that Li be intercalated into BN by means of MM.

However, after ball milling of h-BN and other medium, borides and/or nitrides are generally formed, e.g. for BN–Ti system formed δ-TiNχ [15] or TiN and TiB_2 [16], for BN–Fe formed ε-FeχN [17], and for BN–Al produced Al–B–N solid solution [18]. In case of BN–Al system, milled BN–Al formed AlB_2 and AlN after heat treating. Pure h-BN mainly transformed into amorphous [19–22] or turbostratic BN [23–25].

The purpose of this study is then to investigate the effects of ball milling and post-annealing on h-BN/Li mixing state and phase formation. Particularly, it is interesting to see where Li is intercalated into h-BN, or boride and/or nitride are formed with lithium. The crystal structure of synthesized compounds will be discussed in detail.

2. Materials and methods

The starting materials are h-BN with thin plate-like morphology (purity up to 99.5%, Fig. 1, NACALAI TESQUE, INC.) and lithium metal (purity up to 99.9999%, KOJUNDO CHEMICAL Lab., CO., LTD). Li was cut into a stick shape with dimension of 1 mm in length, 0.5 mm in thickness and width using a knife, from a bar-shaped Li bulk after removing the oxide scale on the surface though it was kept in Ar atmosphere. In this study, the samples were kept and treated in a glove box filled with argon gas (purity up to 99.9999%). A vibratory ball mill (NISSIN GIKEN Corporation, Super Misuni NEV-MA8, 710 rpm) was used for mechanical milling. The 3 g of Li and BN mixture with the molar ratio of 1: 2.2 (the weight ratio of 1: 7.9 from volume ratio of 1: 2) and 9 AISI 304 balls (about 3.58 g per a ball) were set in a stainless vessel under argon atmosphere. After ball milling, the sample was subjected to heat treatment at 700 °C for 2 h in argon atmosphere.

The samples prepared were characterized by X-ray diffractometry (XRD, RIGAKU Corporation, RINT-2100, Cu-K_α radiation). To carry out XRD in Ar atmosphere, the samples were sealed in an airtight sample holder equipped with beryllium window.

The thermal analysis of the samples was investigated by TG-DTA (Thermo Gravimetric - Differential Thermal Analysis, RIGAKU Corporation, Thermo Plus 2 series TG8120) with a heating rate of 10 °C/min in a flowing argon atmosphere from room temperature to 700 °C.

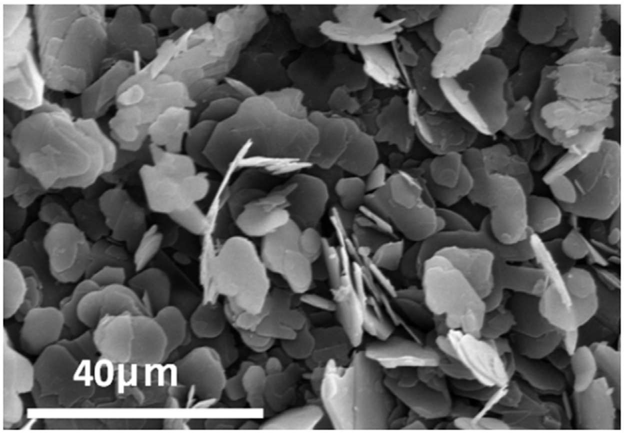

Fig. 1. SEM (scanning electron microscope) image of pure h-BN powder.

Li state in the heat-treated samples was examined by ^{7}Li NMR (nuclear magnetic resonance). NMR measurements were carried out under 4.65 T of magnetic field by using a standard phase coherent-type NMR pulsed spectrometer. Free induction decay (FID) signal was observed after a single pulse of 20 μs at room temperature. NMR spectra were measured by the fast Fourier transform (FFT) method of the FID. The samples for NMR were prepared by sealing in glass tubes in argon atmosphere and measured at 76.94 MHz with a repetition time of 6–75 s determined by the longitudinal relaxation times. LiCl aqueous solution was used as a reference.

Also, Rietveld method was conducted for structural analysis of heat-treated samples using RIETAN-FP [26].

3. Results

Fig. 2 shows the results of XRD after ball milling h-BN with lithium for different milling times. The BN peaks, especially (002), become broader and smaller with increasing milling time. The Li (110) peak disappears when milling time was more than 10 h.Very small Li_3N peaks can be seen when the milling time is longer than 5 h (Fig. 2 (b)), but all peaks disappear after 60 h of milling time due to amorphization.

A small amount of Li possibly reacts with nitrogen atoms from BN by mechanical activation. It can be considered that the Li_3N formation might be due to the reaction between Li and air from adsorbed gas molecules on the ball mill container and the balls, or through inflowing. However, Li_2O, Li_2O_2 or Li_2CO_3 would be produced if Li reacts with air because the reactivity of O_2 with Li is higher than that of N_2 [27]. Thus, there is another possibility for activated Li and h-BN during ball milling. Streletskii et al. [19] and Gasgnier et al. [25] reported possible reaction of h-BN with H_2O when ball-milled h-BN is exposed to air because the mechanical milling increases the reactivity of h-BN. Also, the Li_3N formation strongly depends on the milling temperature, namely cooling-water temperature of milling machine. It was observed even after 2.5 h of milling time when the milling was carried out under relatively high ambient temperature. It can be said there is no intercalation during ball-milling.

Fig. 3 shows the XRD patterns of the milled samples after heat treatment. New peaks appeared after the heat treatment except for the sample milled for 60 h. These new peaks can not be identified with the reported peaks for lithium borides or lithium nitrides. They are rather similar to Li-BNICs reported by A. Sumiyoshi et al. [6], indicating formation of a new phase through the mechanochemistry and heat treatment even in Li–BN system. The Li–BN system exhibits different tendency from Al–BN systems, where milling h-BN with Al would produce AlB_2 and AlN after heat treating [18].

To investigate the reaction during heat treatment of the milled samples, DTA was carried out. The DTA curves of the milled samples for several durations are shown in Fig. 4. The samples milled for 0, 1 and 2.5 h exhibit an endothermic peak around 180 °C representing lithium melting. It means that metallic Li is remained in the samples milled for less than 2.5 h. Clear exothermic peaks between 200 and 500 °C are also seen (except for 60 h milling), which must be involved with Li atoms in the milled samples because milled BN only does not exhibit any DTA peak. In order to understand whether these peaks correspond to synthesis of Li-BNICs or not, the samples milled for various milling time periods were heat-treated at several temperatures (350–700 °C). As the representative result, the XRD profiles for the sample milled for 2.5 h are shown in Fig. 5 (a), and the peak area and FWHM (full width at half maximum) at (002)