Solid State Sciences 47 (2015) 68–72

Contents lists available at ScienceDirect

Solid State Sciences

journal homepage: www.elsevier.com/locate/ssscie

Good reproductive preparation method of Li-intercalated hexagonal boron nitride and transmission electron microscopy – Electron energy loss spectroscopy analysis

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ARTICLE INFO

Article history:
Received 5 November 2014
Received in revised form
25 April 2015
Accepted 27 April 2015
Available online 28 April 2015

Keywords:
Hexagonal boron nitride
Alkali metal intercalation
X-ray diffraction
Electrical conductivity
Transmission electron microscopy
Electron energy loss spectroscopy

ABSTRACT

A Li-intercalated hexagonal boron nitride (Li-h-BNIC) phase was synthesized using a highly reproducible method that involves annealing an Li_3N and h-BN mixture at 1220 K. Powder X-ray diffraction, electrical conductivity measurements, transmission electron microscopy (TEM) and electron energy loss spectroscopy were performed. The stacking of BN atomic layers in the Li-h-BNIC phase is not the same as the two-layer stacking periodicity of h-BN. TEM observation suggests the existence of incommensurate periodicity along the intralayer direction. From the low-loss and core-loss spectra, the Li-h-BNIC phase is not metal as predicted by the first-principle calculations. Satellite peaks of 1 s to π^* transition in the B *K*-edge core-loss spectrum indicate the presence of N atom vacancies modified by O atoms in the h-BN atomic layer.

1. Introduction

Hexagonal boron nitride (h-BN) has a stacking structure of 2D boron nitride atomic layers analogous to graphite. Intercalation into the interlayers of h-BN to change the material properties is of similar interest to graphite intercalation compounds (GICs) [1]. Recently, theoretical studies were performed on h-BN intercalation compounds (h-BNICs). The possibility of alkali–metal h-BNICs with metallic characteristics has been predicted by first-principles calculations [2,3]. Alkali metal GIC-like structures without defects or curvature in the h-BN atomic layer were assumed in these two studies. Oba et al. reported the possibility of inducing an impurity level in the wide band gap of h-BN by the “dilute” intercalation of donor alkali metal atoms or acceptor F atoms [4]. Several experimental studies investigating h-BN intercalation compounds have been carried out. Doll et al. reported K intercalation into h-BN thin films and a $(2 \times 2)R0^\circ$ super lattice structure commensurate with the h-BN parental lattice using transmission electron microscopy (TEM) analysis [5]. However, super lattice diffraction can only be observed by TEM prior to K de-intercalation. Sakamoto et al. reported Br_2 and Cs intercalation into h-BN using the two-zone method [6]. The mass fraction of intercalates is at most 2% and Cs islands were observed by dark field TEM. Neither Doll nor Sakamoto performed X-ray diffraction (XRD) analysis. Shen et al. reported bulk-scale preparation of SO_3F-h-BNIC and verified the metallic characteristics of the compound using electrical conductivity measurements [7]. Kovtyukhova et al. reported the reversible intercalation of Brønsted acids into h-BN without covalent bonding [8].

Intercalation of layered materials, such as h-BN, is interesting both for the study of fundamental property changes that result from intercalation and from a materials science perspective as a wide band-gap material. However, there have been relatively few experimental reports on the preparation of h-BNIC. In particular, there have been very few studies investigating the preparation and properties of alkali metal h-BNIC. We have successfully produced XRD-scale Li-h-BNIC and reported on the differences between the crystal structure of Li-h-BNIC and the parent h-BN phase [9,10]. In our previous studies analysis of the Li-h-BNIC phase was difficult because of the low reproducibility of the phase. Here, we report on a preparation method of Li-h-BNIC with high reproducibility and present TEM and electron energy loss spectroscopy (EELS) analysis

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http://dx.doi.org/10.1016/j.solidstatesciences.2015.04.011

of the electronic structure. We also report electrical conductivity measurement and reanalysis of XRD data.

2. Experimental

Li-h-BNIC was prepared by mixing Li_3N powder (Sigma–Aldrich, 99.5%) and h-BN powder (high-purity materials, 99%up) using an agate mortar in an Ar-filled glove box with a molar ratio $Li_3N/BN = 0.3–1.1$. The starting mixture was sealed into a stainless steel tube using arc welding. The welded stainless steel tube was annealed at a temperature ranging from 700 K to 1500 K for 10 h in an electric furnace. The annealed tube was opened in an Ar-filled glove box. The different phases present in product materials were identified using X-ray powder diffraction with Cu Kα radiation (Rigaku Co., SmartLab). Electrical conductivity measurements were performed on pellets of the product powders using the van der Pauw method (TOYO corporation, Resitest 8300) at temperatures ranging from room temperature to 400 °C under vacuum conditions maintained by an oil rotary pump. The sample pellets for electrical conductivity measurement were prepared by spark plasma sintering (SPS) (Fuji Electronic Industrial Co., SPS-515S) at 720 °C for 30 min. TEM observation and electron diffraction measurements of Li-h-BNIC and pristine h-BN were conducted using a JEOL JEM-2010. High-energy-resolution EELS measurements were performed under a monochromator analytical TEM [11]. B *K*-edge core-loss and low-loss spectra were obtained. The energy resolution was 80 meV for the low-loss spectroscopy and 0.15 eV for the core-loss spectroscopy. Rietveld analysis of the powder XRD pattern was performed using RIETAN-FP software [12].

3. Results and discussion

Fig. 1 shows the XRD patterns of samples having molar ratios $Li_3N/BN = 0.3, 0.5, 0.7, 1.1$ at 1220 K. The powder XRD patterns indicate that the samples are composed of Li-h-BNIC, alfa-Li_3BN_2 and Li_2O. The existence of the Li_2O phase could be due to relatively low purity of the starting reagent and the atmosphere not being completely inert. The XRD pattern of the Li-h-BNIC phase observed here is similar to the pattern observed from material synthesized from a mixture of Li and h-BN in our previous reports [9,10]. The XRD pattern of the Li-h-BNIC phase is almost identical to the XRD pattern from the Li-h-BNIC phase analyzed by Yamane et al. [13]. However, the intensity of minor peaks of the Li-h-BNIC phase reported by Yamane et al. ($2\theta = 33.8°, 40.4°, 43.7°, 43.9°$ [13]) was not observed in the present Li-h-BNIC phase. Based on the 2θ values reported by Yamane et al., the minor peaks were likely derived from Li_2O or α-Li_3BN_2. In our previous study, Li-h-BNIC was obtained in only three of 10 trials conducted under the same conditions for the Li metal and h-BN reaction [9]. In the present study, Li-h-BNIC was successfully obtained in each of the 10 trials. The reproducibility of the Li-h-BNIC has improved considerably using the method described in this work. Furthermore, the yield in Ref. [9] was only 20 wt%, while the yield is 70 wt% in the present work. The exact composition of the Li-h-BNIC is still unknown because a single-phase Li-h-BNIC sample could not be produced.

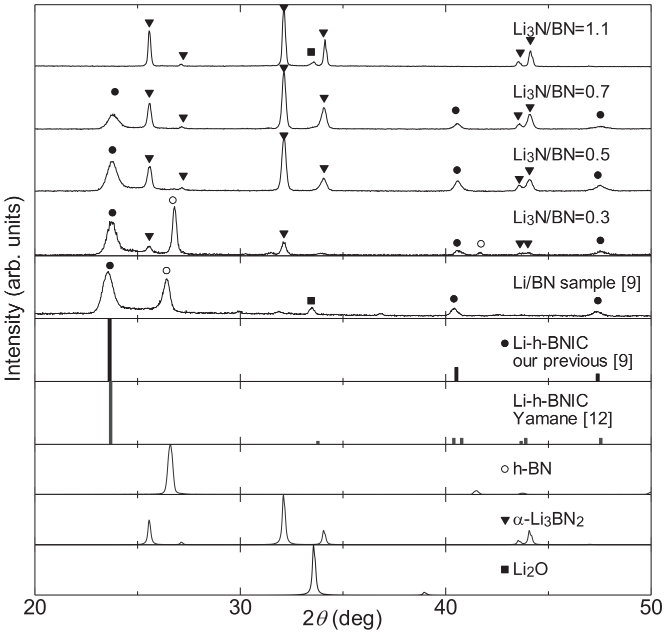

Fig. 1. Powder XRD patterns recorded from samples with molar ratios $Li_3N/BN = 0.3, 0.5, 0.7, 1.1$ at 1220 K and reference compounds Li/BN sample [9], Li-h-BNIC [9], Li-h-BNIC [13], h-BN, α-Li_3BN_2, and Li_2O.

TEM analysis was performed using a powder sample synthesized with an ingredient ratio of $Li_3N/BN = 0.5$. Fig. 2 shows the diffraction pattern of the Li-h-BNIC phase ([1000] direction of incidence) and the simulated diffraction pattern from an h-BN structure with an *a*-direction expansion of 2.48% and a *c*-direction expansion of 12.86%. The expansion ratios were examined in our previous report [10]. In the present study, a split spot diffraction pattern was observed in the Li-h-BNIC phase, as well as the previously reported Debye–Scherrer ring-like diffraction pattern [10]. The split direction is the intralayer direction of the h-BN atomic layer. The distance between the split spots corresponds to approximately eight times the *a*-direction lattice constant of the expanded h-BN structure, 2.566 Å. This indicates the presence of an intralayer direction with incommensurate structure. This incommensurate periodicity likely originates from the stacking change of the BN atomic layers and interlayer Li atoms. This split spot diffraction pattern changed into a Debye–Scherrer ring pattern by intentionally irradiating the sample with an electron beam at a higher voltage than that used for observation. The 10–11 diffraction spot in Fig. 2 (b) is not present in Fig. 2 (a). This can be interpreted as loss of the two-layer stacking periodicity of the pristine h-BN structure due to the imperfect Li intercalation into the h-BN interlayer. In this paper, we will use the abbreviations "2L model" to indicate the two-layer stacking periodicity structure of pristine h-BN and "1L model" to indicate the structure without the two-layer stacking periodicity. Because the 0001 diffraction spot is not present in the 2L model, the 0002 diffraction spot in the 2L model should be reconsidered as a 0001 diffraction spot in the 1L model. Using this interpretation, the 10–12 diffraction spot of the 2L model should be reconsidered as the 10–11 diffraction spot in the 1L model, and the 10–11 diffraction spot in the 2L model disappears in the 1L model. The disappearance of the 10–11 diffraction spot in the 2L model was confirmed by XRD. We also re-conducted the previously reported Rietveld analysis of the powder XRD pattern [10] using the 1L model of Li-h-BNIC.

Fig. 3 (a) shows the Rietveld fitting of the XRD pattern reported in Ref. [10] using the 1L model of Li-h-BNIC and (b) shows the Rietveld fitting of the 2L model of Li-hBNIC. The arrangement of Li atoms is assumed as a stage-1 MC_6 system. The stacking sequence of BN sheets, which is described in terms of *ABAB* for pristine h-BN, is assumed as $A\alpha A\alpha$ for the 1L model and $A\alpha B\alpha$ for the 2L model. The used lattice parameters were based on an h-BN structure with an *a*-direction expansion 2.48% and c-direction expansion 12.86% refined in our previous report [10]. The lattice parameters of the used structure models are $a = 4.4437$ Å, $c = 3.7599$ Å, space group 174 for the 1L model and $a = 4.4437$ Å, $c = 7.5198$ Å, space group 173 for the 2L model. The *c* value of the 2L model is twice that of the 1L