



Letter

Optical band gap and disordered structure in Li_8GeN_4 H. Aoyama^a, S. Kuwano^a, K. Kuriyama^{a,*}, K. Kushida^b^a College of Engineering and Research Center of Ion Beam Technology, Hosei University, Koganei, Tokyo 184-8584, Japan^b Department of Arts and Sciences, Osaka Kyoiku University, Kashiwara, Osaka 582-8582, Japan

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ABSTRACT

The band gap and disordered structure in Li_8GeN_4 (lattice constant: 9.622 Å) are studied by optical absorption, photoacoustic spectroscopy, X-ray diffraction, and Raman scattering spectroscopy. Li_8GeN_4 is a semiconductor with the band gap of 2.61 eV, suggesting the transition from the N-2p valence band to the conduction band mainly consisting of Ge-4s and/or -4p orbitals. A broad Raman peak is observed at 530 cm^{-1} , indicating the homogeneously random distribution of Li and Ge atoms. A possible distribution of Li and Ge is proposed. Li_8GeN_4 crystallizes in a superstructure of eight face-centered N sublattices. In each sublattice, one Li and one Ge atoms are randomly and diagonally occupied at two tetrahedral sites next to N, while six Li atoms reside at the other six tetrahedral sites next to N. The possible locations of one remaining Li atom are also discussed.

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1. Introduction

Wurtzite GaN has attracted enormous numbers of researchers' interests because of its potentials to be used in optical devices, while zinc-blende (ZB) GaN [1] is metastable. LiZnN (space group: $F-43m$, see Fig. 1a) [2,3] can be viewed as a ZB GaN-like $[\text{ZnN}]^-$ lattice whose interstitial sites are partially filled with He-like Li^+ ions [2,3], leading to an ordered filled tetrahedral semiconductor as an alternative to ZB GaN. According to the "interstitial insertion rule" by Zunger's group [3–5], the insertion of Li^+ into the interstitial sites in $[\text{ZnN}]^-$ causes an upward shift in the X point of the conduction band, which exposes the Γ point as the conduction band minimum and converts indirect band gap materials into direct ones. However, the optical band gap (1.91 eV) [2] of LiZnN is much smaller than that (3.27 eV [6,7]) of ZB GaN. Furthermore, Zn in LiZnN can be hypothetically "transmuted" into two types of isovalent pair ($\text{Ga}_{0.5} + \text{Li}_{0.5}$) and ($\text{V}_{0.25} + \text{Li}_{0.75}$), resulting in $\text{Li}(\text{Ga}_{0.5} + \text{Li}_{0.5})\text{N}$ and $\text{Li}(\text{V}_{0.25} + \text{Li}_{0.75})\text{N}$ lattices, respectively. As shown in Fig. 1b and c, the isovalent cation pairs (Li and Ga or V) occupy all the tetrahedral sites surrounded by four N atoms in these lattices, analogous to LiZnN . $\text{Li}_3\text{Ga}_2\text{N}_2$ ($Ia3$) [8–12] and Li_7VN_4 ($P-43n$) [13–16] consist of eight $\text{Li}(\text{Ga}_{0.5} + \text{Li}_{0.5})\text{N}$ and eight $\text{Li}(\text{V}_{0.25} + \text{Li}_{0.75})\text{N}$ lattices, respectively. In comparison with the band gap of ZB GaN, the band gap (4.15 eV) of $\text{Li}_3\text{Ga}_2\text{N}_2$ is large and that (1.46 eV) of Li_7VN_4 is much smaller. In the present study, we paid attention to a new material Li_8GeN_4 which substituted Ga or V for Ge. According to David et al.

[17], Li_8GeN_4 crystallizes in a crystal structure similar to $\text{Li}_3\text{Ga}_2\text{N}_2$ and Li_7VN_4 . As previously reported, the space group of Li_8GeN_4 is $Im-3m$ [17] or $Ia-3$ [18]. However, the atomic distribution in Li_8GeN_4 has not been precisely clarified. Since Li_8GeN_4 possesses more Li atoms than Li_7VN_4 and $\text{Li}_3\text{Ga}_2\text{N}_2$, it would show different features in atomic distributions with Li_7VN_4 and $\text{Li}_3\text{Ga}_2\text{N}_2$. In the present study, the optical absorption of Li_8GeN_4 is interpreted by comparing it with those of Li_7VN_4 and $\text{Li}_3\text{Ga}_2\text{N}_2$. We also propose a possible arrangement of Li and Ge atoms in Li_8GeN_4 by Raman scattering spectroscopy and X-ray diffraction (XRD) analysis.

2. Experimental

Li_8GeN_4 was grown by direct reaction of Li_3N powder (99.5% pure) and Ge (99.999% pure). These two raw materials with the molar ratio $\text{Li}_3\text{N}:\text{Ge}$ of 2.5:1 were inserted in a Ta crucible of 10 mm in diameter and 100 mm in length, and the charged crucible was capped with a Ta cap. The charged crucible was set into a longitudinal resistance furnace inside a stainless steel chamber with a gas inlet on the sidewall. After the chamber was evacuated to the pressure of 10^{-3} Torr, N_2 gas was introduced from the inlet until the inside gas pressure became 700 Torr. The pressure of N_2 gas affects the growth of Li_8GeN_4 , which would be related to the decomposition temperature of Li_3N . If the N_2 pressure is lower than 700 Torr, the synthesized compounds contain Ge and Li–Ge complex materials, which suggests that Li_3N decomposes to Li and N_2 before the reaction among Li, Ge and N occurs. The crucible was heated up to 973 K at the ratio of 40 K/min in the chamber and the temperature was kept at 973 K for 8 h. As-grown samples were polycrystalline and yellow–brown, and showed low thermal and chemical stability, especially, rapid oxidation and hygroscopy.

The structural identification of as-grown crystals was performed by an X-ray diffraction (XRD) analysis and a Raman spectroscopy. A typical powder XRD pattern of as-grown crystals was analyzed using a diffractometer (Rigaku Giga-Flex Rad-C, $\text{Cu K}\alpha$ radiations). A laser Raman spectrophotometer (JASCO NR-1800) was used for

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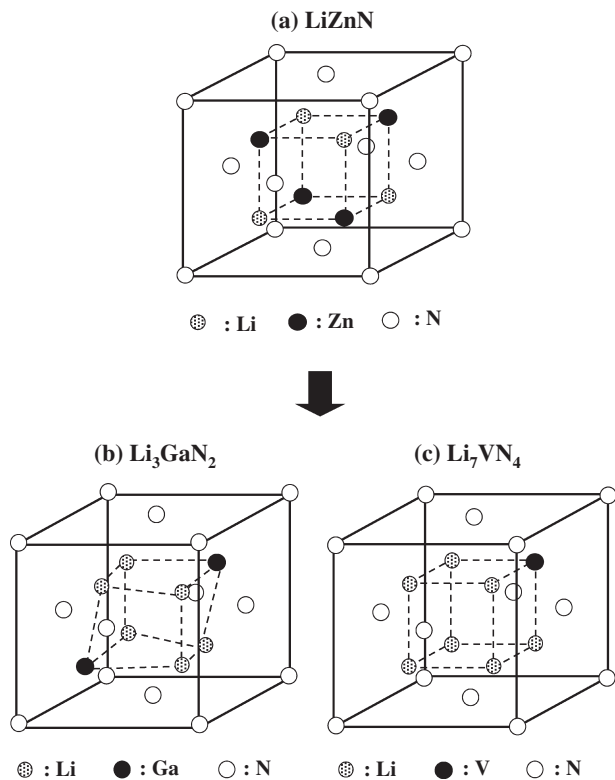


Fig. 1. The unit cell of (a) LiZnN and 1/8-sublattices of (b) Li_3GaN_2 and (c) Li_7VN_4 .

the Raman spectroscopy. The Raman spectra were taken at room temperature in backscattering geometry using a 514.5 nm line of Ar^+ -ion gas laser with a power of 100 mW.

Optical absorption measurements of Li_8GeN_4 were performed using a scanning spectrophotometer (Shimadzu UV-3101 PC) at room temperature. Additionally, a photoacoustic spectroscopy (PAS) method was also applied for clarifying the band gap of Li_8GeN_4 . These methods were used for the measurements of the optical absorption edges of various tetrahedral semiconductors [2,11]. PAS is a useful tool for studying optical absorption of light scattering materials such as powders and polycrystalline samples. PAS is also expected to be applicable to the study of non-radiative process in excited solids, since photoacoustic (PA) signal seems to be related to the nonradiative part of de-excitation or recombination. The PAS system with a 500 W xenon lamp as a light source was used to detect the PA signal. The signal picked up by a microphone was detected through a lock-in amplifier at room temperature. All the spectra were normalized against a carbon black standard. Since PAS is concerned with the amount of absorbed light instead of the reflected or transmitted light, the influence of light scattering effects is greatly reduced. Therefore, the samples for the PAS measurements were obtained by powdering as-grown Li_8GeN_4 .

3. Results and discussion

Fig. 2 shows a typical powder XRD pattern of as-grown crystals. As-grown crystals were confirmed to be a single phase Li_8GeN_4 with a lattice constant of 9.622 Å, which is consistent with the one reported in the previous report [17] and the JCPDS data [18]. The lattice parameter of Li_8GeN_4 is close to those of Li_3GaN_2 (9.605 Å) [10] and Li_7VN_4 [15]. Furthermore, the XRD pattern of Li_8GeN_4 is similar to those of Li_3GaN_2 and Li_7VN_4 , since almost all the diffractions observed by Li_8GeN_4 also appear in those by Li_3GaN_2 and/or Li_7VN_4 . Thus, the XRD data supports that the crystal structure of Li_8GeN_4 is close to those of Li_3GaN_2 and Li_7VN_4 .

Fig. 3 shows typical optical absorbance spectra of Li_8GeN_4 samples and GaP as a reference. The absorbance curve of Li_8GeN_4 showed an abrupt increase at 525 nm (2.36 eV) and then saturated at 475 nm (2.61 eV), after the absorbance gradually increased from 750 nm. The GaP reference samples showed a saturation of optical

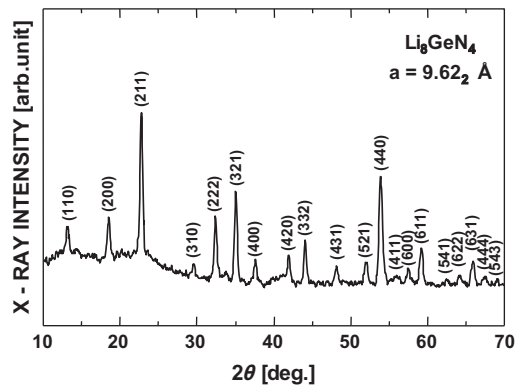


Fig. 2. Typical X-ray powder diffraction pattern of Li_8GeN_4 .

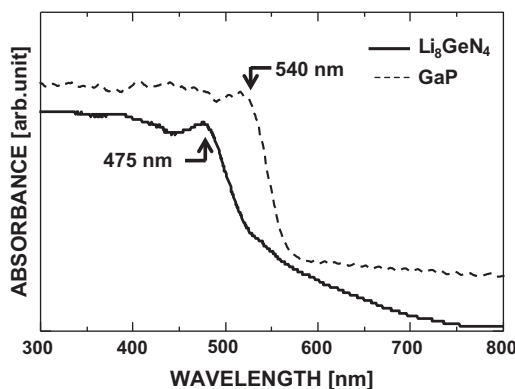


Fig. 3. Optical absorbance spectra of Li_8GeN_4 (solid line) and GaP (dotted line) as a reference.

absorbance at 540 nm (2.29 eV) which is consistent with the band gap of 2.27 eV. The situation of Li_8GeN_4 is similar to that of GaP, which indicates that the band gap of Li_8GeN_4 exists at 2.61 eV. The gradual increase in the absorbance of Li_8GeN_4 would originate from crystal imperfections such as impurities and/or defects introduced during the synthesis of Li_8GeN_4 . Fig. 4 shows the PAS spectrum of Li_8GeN_4 . The PA signal of Li_8GeN_4 showed a steep increase at around 490 nm (2.53 eV) after the PA signal gradually increased from 550 nm. The PAS measurements suggest that the optical absorption of Li_8GeN_4 begins at around 490 nm, which is supported by the PAS spectrum of GaP because of a steep increase also observed at around the absorption edge of GaP. Accordingly, from the optical absorption and the PAS measurements, the band gap of Li_8GeN_4 is determined to be 2.61 eV. In previous studies, we studied the electronic structures of Li_7VN_4 [15] and Li_3GaN_2 [10,12], which clarified that Li_7VN_4 was a narrow gap semiconductor with the energy gap of 1.4 eV between the V-3d related conduction band and the N-2p valence band [15], while Li_3GaN_2 was a wide gap semiconductor with the band gap of 4.15 eV between the Ga-4s related conduction band and the N-2p valence band [10,12]. The band gap of Li_3GaN_2 (Li_7VN_4) would be mainly determined by the electronic structure based on GaN_4 (VN_4) tetrahedra. Therefore, the optical absorption in Li_8GeN_4 would also result from the transition from the N-2p valence band to the conduction band mainly consisting of Ge-4s and/or -4p orbitals. The band gap of Li_8GeN_4 is smaller than the experimental band gap of Li_3GaN_2 (4.15 eV) [11], while it is larger than that of Li_7VN_4 (1.4 eV) [15]. This reflects that the Ge related conduction band in Li_8GeN_4 is located nearer to the N-2p valence band than the Ga-4s related conduction band in Li_3GaN_2 , as the result of the replacement of Ga in

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