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Optical band gap of the filled tetrahedral semiconductor LiZnN

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The optical band gap of the filled tetrahedral semiconductor LiZnN [viewed as a hypothetical zinc-blende $(ZnN)^-$ lattice partially filled with He-like Li^+ interstitials] was studied. The band-gap nature of LiZnN predicted theoretically by an *"interstitial insertion rule"* is confirmed to be *direct* with a forbidden gap of 1.91 eV at room temperature. The band gap is closer to a value calculated using a nonrelativistic augmented-spherical-wave method rather than that predicted from the empirical trend of band gaps between the filled tetrahedral (LiZnAs and LiZnP) and zinc-blende (GaAs and GaP) structures. The difference on the bonding character between the filled tetrahedral and zinc-blende compounds is discussed.

The band-structure modification of diamond and zinc-blende semiconductors has been tested theoretically by insertion of small atoms such as H and He at their tetrahedral interstitial sites.[1,2] We encounter technological difficulties for insertion of small atoms at tetrahedral interstitial sites of diamond and zinc-blende structures even if one used techniques such as ion implantation and molecular-beam epitaxy. However, Wood, Zunger, and de Groot aimed at ternary compounds[2] referred to as "filled tetrahedral compounds." A filled tetrahedral semiconductor LiZnP is viewed as a hypothetical zinc-blende compound $(ZnP)^-$ partially filled with He-like Li^+ interstitials. The band-gap nature of LiZnP predicted theoretically by an "interstitial insertion rule"[2] was confirmed to be *direct* with a *wide* band gap[3] of 2.04 eV at room temperature. This rule has been applied[4] to a new material LiZnN, which is viewed as a hypothetical zinc-blende-like $(ZnN)^-$ lattice partially filled with He-like Li^+ interstitials. Although the hypothetical cubic compounds, $(ZnP)^-$ and $(ZnAs)^-$, are analogous to the real compounds GaP and GaAs, respectively, the hypothetical zinc-blende compound $(ZnN)^-$ is not viewed as the real GaN, because the latter crystallizes at low pressures in the *wurtzite* structure with a direct principal band gap of 3.36 eV. The calculated band structure[4] of $(ZnN)^-$ for the same lattice constant ($a_0 = 4.877$ Å) as LiZnN (Ref. 5) shows a direct band gap of about 0.8 eV. Therefore, it is very important to confirm experimentally the band-gap nature of LiZnN to clarify whether the interstitial insertion rule is applied to LiZnN.

The crystal structure (Fig. 1) of LiZnN is viewed as follows: Whereas the zinc-blende structure of a D^{III}-C^{V} compound (e.g., GaAs) has the D^{III} atom at $\tau_1 = (0,0,0)a_0$ (where a_0 is the lattice parameter), the C^{V} atom at $\tau_2 = (\frac{1}{4},\frac{1}{4},\frac{1}{4})a_0$, and two empty interstitial sites at $\tau_3 = (\frac{1}{2},\frac{1}{2},\frac{1}{2})a_0$ (next to the anion) and $\tau_4 = (\frac{3}{4},\frac{3}{4},\frac{3}{4})a_0$ (next to the cation), one could "transmute" D^{III} into its isovalent pair B^{II}-A^{I} (e.g., Ga into Zn+Li) and distribute these atoms among τ_1, τ_2, and τ_3 sites. These sites for LiZnN are occupied by Zn, N, and Li atoms, respectively, while the τ_4 site is empty. LiZnN belongs to the antifluorite structure[6] (the broken line in Fig. 1), while the space group of LiZnN is $F\bar{4}3m$ as well as a zinc-blende structure. Zn and Li are coordinated by four N atoms, respectively, but N is eightfold coordinated with four Zn and four Li nearest neighbors.

In this paper we give the optical band gap of LiZnN. We find that LiZnN is a *wide*-gap semiconductor with a *direct* forbidden band gap of 1.91 eV. This band-gap nature is consistent with that predicted by the interstitial insertion rule.

The LiZnN samples used in this study were presented by direct reaction between NH_3 and LiZn. The LiZn alloy was grown by direct melting of equimolar amounts of Li (99.9% pure) and Zn (99.9999% pure), as reported ear-

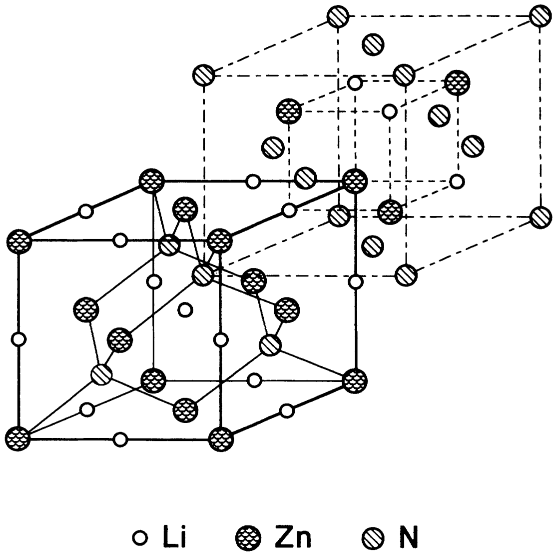

FIG. 1. Crystal structure of the filled tetrahedral semiconductor LiZnN (space group: $F\bar{4}3m$). The ternary antifluorite structure is depicted by the broken line. Note that Zn and Li are coordinated by four N atoms, respectively, but that N is eightfold coordinated with four Zn and four Li nearest neighbors.

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lier.[7] After several plates ($7\times7\times1$ mm^3 in size) of LiZn alloy were charged on the Mo boat in a quartz tube, plates were heated to a desired temperature in N_2 flow. LiZn plates were subsequently annealed in NH_3 flow at around 490 °C for 5 h. The grown crystals were polycrystalline with bright deep red color under illumination using a tungsten lamp and showed rapid oxidation and hygroscopy. As-grown crystals were brittle. The typical x-ray-powder-diffraction pattern consisting of the single phase LiZnN is shown in Fig. 2. As-grown crystals sometimes contained lithium amid ($LiNH_2$) (Ref. 8) and Li_2O as contaminants. The lattice constant was estimated to be $a_0=4.910\pm0.005$ Å, which value is slightly larger than the previously reported value ($a_0=4.877\pm0.002$ Å).[5] This may be attributed to the slight deviation from the stoichiometry.

The optical measurements were carried with a similar method to that used for $LiInS_2$ single crystals[9] using a scanning spectrophotometer (Shimadzu UV-3101 PC). The optical transmission of LiZnN was measured at 300 K using unpolarized light at normal incidence in the photon wavelength range 500–1200 nm. A typical transmission curve is shown as a function of wavelength in Fig. 3. The fundamental absorption edge lies at around 620 nm. The inset shows the absorption coefficient near the absorption edge. The sample thickness used here was 230 μm. In order to test the band-gap nature, we plotted two relations,[10] $\alpha h\nu = A(h\nu - E_g)^{1/2}$ as a direct material and $\alpha h\nu = B(h\nu - E_g)^2$ as an indirect material (see Fig. 4). Although the curve of $(\alpha h\nu)^{1/2}$ vs $(h\nu - E_g)$ for an indirect band gap contains a linear portion as shown in Fig. 4, the curve is linear over only a very small photon energy range. Furthermore, the curve over the wavelength ranges above ~670 nm (~1.85 eV) must reflect the absorption due to defects such as residual impurities. This situation is observed in an absorption coefficient over the photon energy ranges below ~1.9 eV (see the inset in Fig. 3). Therefore we believe that absorption data obey the relation of directness rather than that of indirectness. When the linear portion of the plot is extrapolated to $\alpha=0$, the direct band gap E_g is estimated to be 1.91 eV with the factor A of 4.94×10^2 cm^{-1} eV$^{-1/2}$. The band-gap directness is explained by the interstitial insertion rule as follows:[4] Insertion of Li^+ at the τ_3 site (next to the anion) of the zinc-blende-like $(ZnN)^-$ structure raises the energy of X_1 of the Brillouin zone. Since the Γ_1 state has significant amplitude at τ_3 site, substitution at τ_3 raises the energy of Γ_1. However, since the conduction bands at X for zinc-blende compounds have relatively much more interstitial charge than do those at Γ_1, the former are more strongly perturbed by interstitial substitutions than are the latter. As a result the degree of band-gap directness increases by closed-shell atom substitution of the τ_3 site, indicating a larger band gap than that of the hypothetical zinc-blende compound $(ZnN)^-$ [$E_g \sim 0.8$ eV; see Fig. 2(b) in Ref. 4]. Therefore, the prediction of band-gap directness due to the interstitial insertion rule is consistent with the band-gap nature evaluated by the present study. Although the observed band gap of LiZnN is smaller than that of GaN (3.36 eV at 300 K), the band gap is closer to a value [about 1.5 eV; see Fig. 2(a) in Ref. 4] calculated using a nonrelativistic

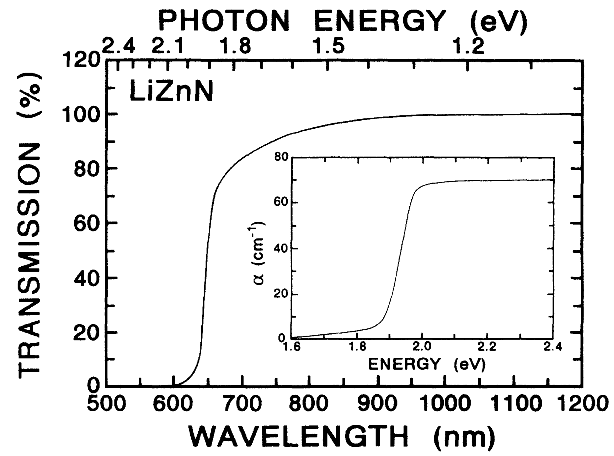

FIG. 3. Typical transmission spectrum of LiZnN (thickness $t=230$ μm). The inset shows the absorption coefficient near the absorption edge.

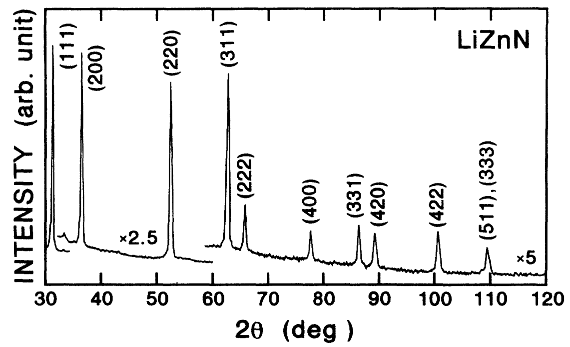

FIG. 2. Typical x-ray-powder-diffraction pattern of LiZnN, which crystallizes in the ternary antifluorite structure with $a_0=4.910\pm0.005$ Å.

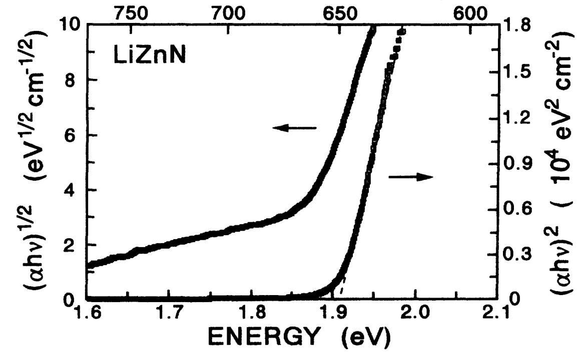

FIG. 4. Plots to test two relations, $(\alpha h\nu)^2$ vs $h\nu$ as a direct material and $(\alpha h\nu)^{1/2}$ vs $h\nu$ as an indirect material, for LiZnN near the fundamental absorption edge at 300 K.

augmented-spherical wave method.[4] Moreover, the observed value is smaller than a value (2.6–3.0 eV) predicted from the empirical trend[3] of band gaps between the filled tetrahedral (e.g., LiZnAs ($E_g = 1.1$ eV from electrical resistivity[11] and 1.25 eV from optical absorption[12]) and LiZnP [$E_g = 2.04 \pm 0.01$ eV (Ref. 3) and 2.1 eV (Ref. 12) from optical absorption]) and zinc-blende [e.g., GaAs ($E_g = 1.42$ eV) and GaP (2.26 eV)] structures. The band gaps for the filled tetrahedral compounds are reduced by 10–20% from the zinc-blende structures. Since the zinc-blende III-V materials are fourfold coordinated, the total-energy gap[13] E_g ($= E_h + iC$) is determined principally by a III-V bond, where E_h represents the average energy gap produced by a potential V_{covalent} and C represents the magnitude of the energy gap produced by a potential V_{ion}. Whereas, since the filled tetrahedral I-II-V compounds are eightfold coordinated with four I and four II nearest neighbors, the band gap of I-II-V compounds is associated with the bonding character of two kinds of bonds, namely, I-V and II-V bonds. A recent Raman-scattering study[14] pointed out that LiZnP reveals the relatively high ionicity of the Li-P bond and the relatively high covalency of Zn-P bond in the *same structure.* Compared with GaN, the relatively small band gap of LiZnN may be attributed to the relatively high covalency of Zn-N bond exceeding the ionicity of Li-N bond, keeping a cubic phase without a phase transition to wurtzite structure. Although for III-V semiconductors C is nearly always less than E_h and the bond is predominantly covalent, GaN with wurtzite structure has a same value of $E_h = C = 7.64$ eV corresponding to the ionicity $f_i = 0.5$.[13]

In conclusion, we found that a filled tetrahedral semiconductor LiZnN is a *wide*-gap semiconductor with a *direct* forbidden band gap of 1.91 eV by the optical measurements. It was confirmed that the interstitial insertion rule is applied to LiZnN. It is suggested that the relatively small band gap of LiZnN in comparison with GaN is attributed to the relatively high covalency of Zn-N bond exceeding the ionicity of Li-N bond.

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