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Optical band gap of the filled tetrahedral semiconductor LiZnP

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We report on the optical band gap of the filled tetrahedral (Nowotny-Juza) compound LiZnP [viewed as a zinc-blende-like $(ZnP)^-$ lattice partially filled with He-like Li^+ interstitials]. The band-gap nature of LiZnP predicted theoretically by an "interstitial insertion rule" is confirmed to be *direct* with a forbidden gap of 2.04 ± 0.01 eV at room temperature. The typical resistivity, Hall mobility, and electron concentration at room temperature are of the order of 10 Ω cm, 25 cm^2/V sec, and 10^{16} cm^{-3}, respectively. The empirical trend of band gaps between the filled tetrahedral and zinc-blende structures is discussed.

Recently, Wood, Zunger, and de Groot[1] have discussed the susceptibility of zinc-blende semiconductors to band-structure modification by insertion of small atoms at their tetrahedral interstitial sites. Their electronic structure calculation has predicted that LiZnP [viewed as a zinc-blende-like $(ZnP)^-$ lattice partially filled with He-like Li^+ interstitials] is a novel type of *direct*-gap semiconductor, not encountered in any cubic III-V material: Among cubic III-V's, only BP, AlP, AlAs, and GaP have wide band gaps; however, all are *indirect*.

The Nowotny-Juza compounds[2] $A^{I}B^{II}C^{V}$ (e.g., LiZnN, LiZnP, LiZnAs, LiCdP, LiCdAs, LiMgN, LiMgP, LiMgAs, and AgMgAs) will comprise a special class of filled tetrahedral semiconductors: Whereas the zinc-blende structure of a $D^{III}C^{V}$ compound (e.g., GaP) has the D^{III} atom at $\tau_1 = (0,0,0)a$ (where a is the lattice parameter), the C^{V} atom at $\tau_2 = (\frac{1}{4},\frac{1}{4},\frac{1}{4})a$, and two empty interstitial sites at $\tau_3 = (\frac{1}{2},\frac{1}{2},\frac{1}{2})a$ (next to the anion) and $\tau_4 = (\frac{3}{4},\frac{3}{4},\frac{3}{4})a$ (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 the τ_1, τ_2, and τ_3 sites. Nowotny and Backmayer[3] have reported the crystal structure of LiZnP as follows: The τ_1, τ_2, and τ_3 sites are occupied by Zn, P, and Li atoms, respectively, while the τ_4 site is empty. This ternary compound belongs to the antifluorite structure.

In this paper we describe the results of the first optical band gap and electrical resistivity measurements of LiZnP. We find that LiZnP is a wide-gap semiconductor with *direct* forbidden band gap of 2.04 ± 0.01 eV. Using the empirical trend of band gaps between the filled tetrahedral and zinc-blende structures, we suggest that the probable band gap of LiZnN lies around 3.0 eV.

The LiZnP samples used in this study were prepared by direct reaction of equimolar amounts of Li (99.9% pure), Zn (99.999% pure), and P (99.999% pure). As reported earlier,[4] the successful crystal growth of the stoichiometric ratio was achieved by using 4 at.% excess Li and 6 at.% excess P to compensate for evaporation losses. A tantalum crucible was used as a container for the LiZnP. The charged crucible was sealed under 10^{-4} Torr in quartz tube. A vertical resistance furnace was heated up at a rate of 100 °C/h from 200 to 680 °C to promote crystallization. After holding for about 120 h, the furnace was cooled at a rate of 100 °C/h. The grown crystals were transparent red in color and showed rapid oxidation and hygroscopy. As-grown crystals contained several grain boundaries. Standard x-ray diffraction analyses showed the crystals to be single phase, exhibiting the antifluorite structure with $a = 5.765 \pm 0.005$ Å. The diffraction line corresponding to the (420) plane was observed using a Cu *Kα* x ray, not observed in LiZnAs (Refs. 3 and 4) and LiZnP.[3] The diffraction from the (420) plane originates from the structure factor $(f_{Li}+f_{II}-f_{V})^2$ for $h+k+l=4n+2$ (Miller indices h, k, l even), namely $(f_{Li}+f_{Zn}-f_{P})^2 \gg (f_{Li}+f_{Zn}-f_{As})^2$. The (420) plane in LiMgP has been confirmed using Fe *K* x ray.[3]

The electrical resistivity of samples used in optical studies was measured by the Van der Pauw technique.[5] The samples were prepared by the same treatment used for the intermetallic compounds LiAl (Ref. 6) and LiGa (Ref. 7). Ohmic contacts were fabricated by placing small indium pellets between the tungsten probes and sample. The typical resistivity (ρ) is shown in Fig. 1. The activation energy estimated from the slope of the resistivity was about 0.11 eV. This value indicates the existence of the

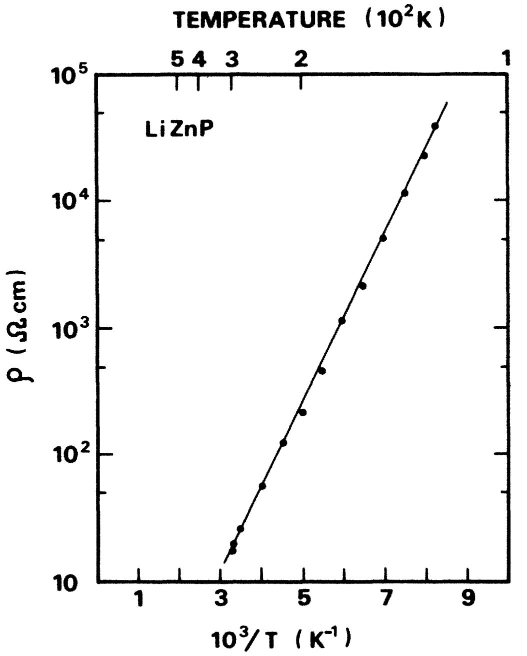

FIG. 1. The temperature dependence of the electrical resistivity of LiZnP used for optical measurements. The activation energy of 0.11 eV indicates the existence of shallow donors.

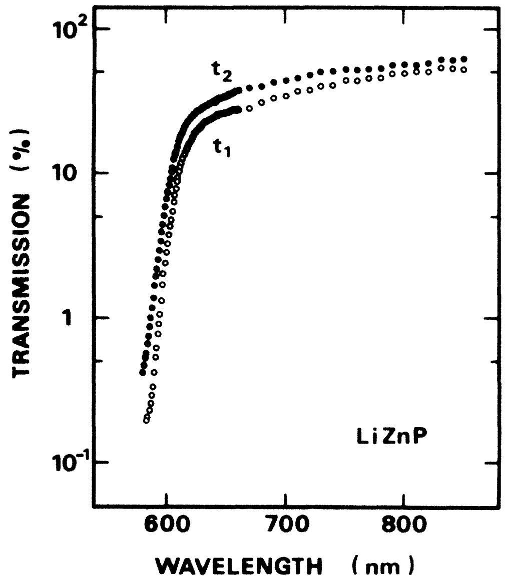

FIG. 2. Transmission as a function of wavelength for two samples with different thickness [t_1 (open circles) $=0.0391$ cm and t_2 (closed circles) $=0.0576$ cm].

shallow donors. Preliminary Hall coefficient measurements at room temperature show the n-type conduction with the Hall mobility (μ_H) of 25 cm^2/V sec and carrier concentration (n) of 2×10^{16} cm^{-3}.

The optical measurements were carried out by the similar method used for the LiInS$_2$ films.[8] The optical transmission of LiZnP was measured at room temperature using unpolarized light at normal incidence in the photon energy range 1.45–2.15 eV. A halogen lamp was used as the optical source. The light chopped at 113 Hz was dispersed by a Ritsu-Oyo-Kogaku MC-2ON monochromator and the output signal was detected by a lock-in amplifier (Brookdeal 9503). Typical transmission curves are shown as a function of wavelength in Fig. 2. The absorption coefficient α can be calculated from the incident light intensity I_0, the transmitted light intensity I, the sample thickness t, and the reflectivity R by means of the relation[9]

$$I \simeq I_0(1-R)^2\exp(-\alpha t).$$

In order to eliminate the unknown parameter R, this relation was estimated from two samples with different thicknesses t_1 and t_2 cut from the same batch by using the relation

$$\alpha(h\nu) = [1/(t_2-t_1)]\ln[I_1(h\nu)/I_2(h\nu)].$$

Figure 3 tests whether the data obey a relation of the form[10]

$$\alpha h\nu = A(h\nu - E_g)^{1/2},$$

which is valid for allowed direct transitions between the simple parabolic bands. When the linear portion of the plot is extrapolated to $\alpha=0$, we find that the direct energy gap E_g is 2.04 ± 0.01 eV and the factor A is 6.73×10^2 cm^{-1}eV$^{-1/2}$. This estimated energy gap lies in the range of values (1.3–2.0 eV) predicted theoretically by the self-consistent local-density approximation pseudopotential total-energy method.[1] The observed band gap is smaller than that of GaP (2.26 eV at 300 K); however, LiZnP has

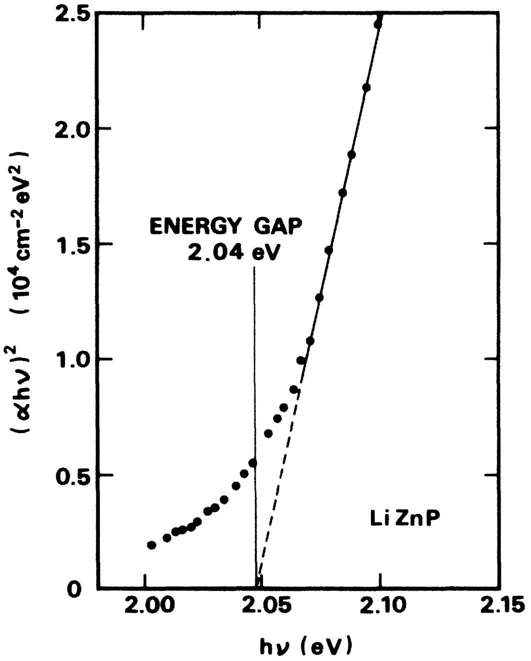

FIG. 3. $(\alpha h\nu)^2$ vs $h\nu$ for LiZnP near the fundamental absorption edge at room temperature. LiZnP has a direct-band gap of 2.04 ± 0.01 eV.

TABLE I. The band gaps (300 K) of the filled tetrahedral (Nowotny-Juza) and III-V compounds. GaN crystallizes into the wurzite structure at low pressures. The probable band gap of LiZnN lies in the range of 2.6–3.0 eV.

Compounds	LiZnAs	GaAs	LiZnP	GaP	LiZnN	GaN
Band gap (eV)	1.1	1.42	2.04	2.26	(2.6–3.0)	3.36
Band-gap ratios	0.77		0.90		···	

become a *direct*-gap material. This indicates that when one inserts Li^+ at the interstitial τ_3 site of the zinc-blende-like $(ZnP)^-$ structure, the X_{3c} conduction band of the Brillouin zone[1] is shifted to higher energies more than the other bands, exposing the Γ_{1c} point as the conduction minimum. Table I shows the empirical trend of band gaps between the filled tetrahedral and zinc-blende structures. Since the band gaps for the Nowotny-Juza compounds [e.g., LiZnP and LiZnAs (1.1 eV)[4]] is reduced by 10%–20% from the zinc-blende structures (e.g., GaP and GaAs), the probable band gap of LiZnN lies in the range of 2.6–3.0 eV with the direct-band gap.[11] These values were estimated using the ratio of the band gaps (see Table I). According to the bonding scheme in LiZnAs discussed by Wei and Zunger,[12] the difference in band-gap value between LiZnAs and LiZnP is interpreted as follows: The directional accumulation of valence charge on the ionic Li–P bond in LiZnP is smaller than that of the ionic Li–As bond in LiZnAs, whereas the extra charge on the covalent Zn–As bond in LiZnAs originating from the residual valence charge of Li is larger than that of the covalent Zn–P bond in LiZnP. As a result, the ionicity of LiZnP overcomes that of LiZnAs. We suggest that an increase in ionicity of $(A^{\rm I}-C^{\rm V})$ bonds and a decrease in covalency of $(B^{\rm II}-C^{\rm V})$ bonds in the same structure are enhanced by replacing a heavier $C^{\rm V}$ element by a lighter one.

In conclusion, we found that the filled tetrahedral compound LiZnP is a wide-gap semiconductor with a *direct* forbidden band gap of 2.04 ± 0.01 eV by the optical measurements. The typical electrical properties of LiZnP were $\rho = 15\ \Omega\,\mathrm{cm}$, $\mu_H = 25\ \mathrm{cm^2/V\,sec}$, and $n = 2\times10^{16}\ \mathrm{cm^{-3}}$ at room temperature. We suggest that LiZnN is likely to be a band gap around 3.0 eV according to empirical trend of band gaps between the zinc-blende and Nowotny-Juza compounds.

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