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Raman scattering from the filled tetrahedral semiconductor LiZnP

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The bonding character in the filled tetrahedral semiconductor LiZnP (space group: $F\bar{4}3m$), viewed theoretically as a zinc-blende-like $(\mathrm{ZnP})^-$ lattice partially filled with He-like Li^+ interstitials, was studied using a Raman-scattering method. Two longitudinal-optical (LO) and transverse-optical (TO) phonons at $\mathbf{k}\sim\mathbf{0}$ (Γ point) for Li-P and Zn-P pairs were observed at 421 and 363 cm^{-1} and 265 and 230 cm^{-1}, respectively. In comparison with the separation of the LO and TO branches at $\mathbf{k}\sim\mathbf{0}$ for each pair, the Li-P bond appears to have relatively high ionicity, whereas the force constant of Zn-P is about 50% higher than that of Li-P, showing the relatively high covalency of Zn-P bond. These results are also supported by the fact that the macroscopic transverse effective charge e_T^* of the Zn-P bond is larger than that of the Li-P bond.

The band-structure modification of filled tetrahedral semiconductors was tested by insertion of small atoms at tetrahedral interstitial sites of diamond and zinc-blende structures.[1,2] The electronic-structure calculation[2] of LiZnP is based on the filled tetrahedral structure viewed as a zinc-blende-like $(\mathrm{ZnP})^-$ lattice partially filled with He-like Li^+ interstitials. LiZnP was predicted to be a *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 and all are *indirect.* The band gap of LiZnP was determined by the optical-absorption measurements.[3,4] We found that LiZnP is a wide-gap semiconductor[5,6] with a *direct* forbidden gap[4] of 2.04±0.01 eV at room temperature, and the band-gap values[7] decrease with temperature, $dE_g/dT=-3\times10^{-4}$ eV/K.

The crystal structure of LiZnP is viewed as follows: Whereas the zinc-blende structure of a D^{III}-C^{V} compound (e.g., GaP) has the D^{III} atom at $\tau_1=(0,0,0)a_0$ (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 LiZnP are occupied by Zn, P, and Li atoms, respectively, while the τ_4 site is empty. LiZnP belongs to the antifluorite structure[8] (see Fig. 1), while the space group of LiZnP is $F\bar{4}3m$ as well as a zinc-blende structure. Zn and Li are coordinated by four P atoms, respectively, but P is eightfold coordinated with four Zn and four Li nearest neighbors. The heteropolar zinc-blende materials do not possess inversion symmetry, so that longitudinal-optical [LO(Γ)] and transverse-optical [TO(Γ)] phonons are not degenerate. Therefore, two LO and TO phonons for Li-P and Zn-P pairs in LiZnP are expected to be observed at $\mathbf{k}\sim0$, as seen in an alloy system[9] $\mathrm{Ga}_x\mathrm{Al}_{1-x}\mathrm{As}$. Furthermore, according to the bonding scheme in LiZnAs discussed by Wei and Zunger,[10] LiZnP would be constructed of a strongly covalent Zn-P bond and a strongly ionic Li-P bond in the *same structure.*

In this paper we describe the results of Raman scattering from the filled tetrahedral semiconductor LiZnP. We found 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* in terms of the separation of the LO and TO branches at $\mathbf{k}\sim\mathbf{0}$ and the difference in the force constant for each bond.

Small red transparent crystals were used in the present study. These crystals were grown by direct reaction of equimolar amounts of Li, Zn, and P, as reported previously.[7] The grown crystals showed gradual oxidation and hygroscopy. Crystals were (111) oriented one consisting of single-crystal domains ~0.1 mm in size. A laser Raman spectrophotometer (JASCO NR-1100) was employed for the Raman measurements. The Raman spectra were excited in backscattering geometry with the 300-mW 514.5-nm line of Ar^+-ion gas laser. A typical

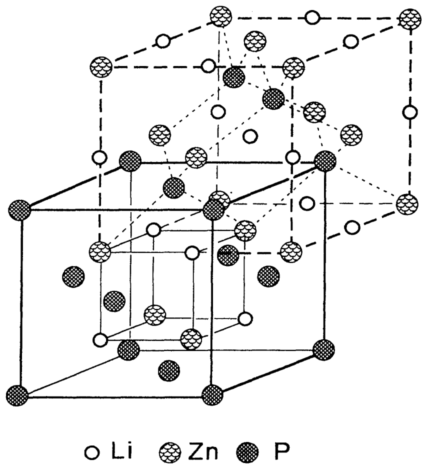

FIG. 1. Crystal structure of the filled tetrahedral semiconductor LiZnP (space group: $F\bar{4}3m$, lattice parameter $a_0=5.765$ Å). The ternary antifluorite structure is depicted by the solid line. Note that Zn and Li are coordinated by four P atoms, respectively, but that P is eightfold coordinated with four Zn and four Li nearest neighbors.

beam spot was $\sim$1 mm Φ. A suitable etchant for LiZnP has not been found yet, so that as-lapped samples were used for the Raman measurements. All measurements were carried out at room temperature.

Figure 2 shows a typical Raman spectrum from a (111)-oriented surface of LiZnP. The four frequency modes were observed at 421, 363, 265, and 230 cm^{-1}. These modes are expected to be associated with LO$_1$ and TO$_1$ (LO$_2$ and TO$_2$) longitudinal- and transverse-optical branches originating from Li-P (Zn-P). Because LiZnP, which exhibits the same space group as a zinc-blende structure, has no inversion symmetry, there will be two first-order Raman peaks corresponding to TO(Γ) and LO(Γ) for each cation-anion pair. Furthermore, one expects that vibrational frequencies involving Li and P should be larger than those for Zn and P, since the frequency difference for Li-P and Zn-P motions is due mainly to the mass difference. Therefore, the Raman peaks observed at 421 and 363 cm^{-1} (265 and 230 cm^{-1}) are assigned as LO$_1$(Γ) and TO$_1$(Γ) [LO$_2$(Γ) and TO$_2$(Γ)] phonons originating from Li-P (Zn-P) pairs. The separation of the LO and TO branches at k$\sim$0 is a measure of ionicity.[11,12] As seen in Fig. 2, the splitting ($\Delta\omega=58$ cm^{-1}) of LO$_1$(Γ) and TO$_1$(Γ) is enhanced more than that ($\Delta\omega=35$ cm^{-1}) of LO$_2$(Γ) and TO$_2$(Γ). From this point of view, the Li-P bond would exhibit higher ionicity in comparison with the Zn-P bond. In zinc-blende-type semiconductors the macroscopic transverse effective charge e_T^* is related to the splitting of the long-wavelength LO and TO phonon modes,[13]

$$e_T^{*2}=(\varepsilon_\infty a_0^3\mu/16\pi)(\omega_{\mathrm{LO}}^2-\omega_{\mathrm{TO}}^2) , \qquad (1)$$

where μ is the reduced mass of the two-component atoms ($\mu^{-1}=m_A^{-1}+m_B^{-1}$), a_0 the cubic lattice constant, and ε_∞ the optical dielectric constant. Assuming that the above equation is valid for ternary compounds, we evaluate e_T^* using the observed ω_{LO} and ω_{TO} values. By substituting $\mu=5.7$ u for Li-P and 21.0 u for Zn-P, $\varepsilon_\infty=9.6$,[14] and $a_0=5.765$ Å into Eq. (1), we obtained $e_T^*=1.56$ for Li-P and 1.84 for Zn-P. The e_T^* value tends to decrease with increasing polarity for a given structure.[15,16] This arises from the reduction in the dynamic charge as the electrons become more tightly bound to the cation. Furthermore, according to Harrison,[15] the ionicity of Phillips and Van Vechten[17,18] is consistent with the square of the polarity. A similar situation has been reported for other Li ternary compounds.[19] Therefore, the relatively high ionicity of the Li-P bond is also supported by the fact that the macroscopic transverse-effect charge[20] of Li-P is less than that of Zn-P.

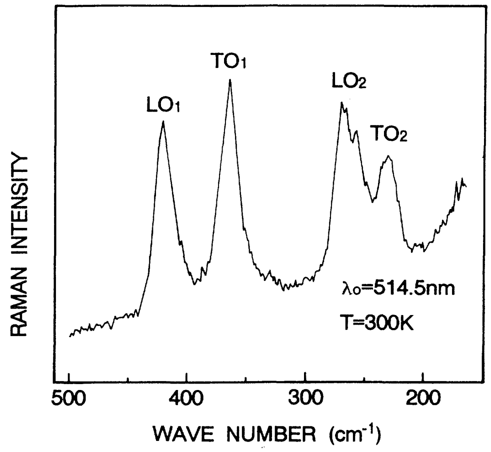

FIG. 2. A typical Raman spectrum of the filled tetrahedral semiconductor LiZnP. The modes TO$_1$ and LO$_1$ (TO$_2$ and LO$_2$) are associated with the transverse- and longitudinal-optical branches originating from Li-P (Zn-P).

The TO-phonon frequency at the Γ point is given by $(C/\mu)^{1/2}$, where C represents force constant of the nearest-neighbor atoms and μ is the reduced mass.[9] Assuming that this relationship is valid for ternary compounds, we evaluate the force constants for each bond. Using 230 and 363 cm^{-1} for the frequencies of the TO phonon at the Γ point of Zn-P and Li-P, respectively, we find that the force constant of Zn-P is about 50% higher[21] than that of Li-P. It has been suggested theoretically that the force constant decreases drastically with increasing bond polarity.[13] This relationship is confirmed experimentally for the tetrahedral binary compounds.[22] Therefore, it is suggested that LiZnP exhibits the relatively high ionicity of the Li-P bond and the relatively high covalency of the Zn-P bond in the *same structure.* This situation is consistent with the difference in the ionicity arising from the splitting of the ω_{LO} and ω_{TO} branches discussed above.

In conclusion, the bonding character of the filled tetrahedral semiconductor LiZnP was studied using a Raman-scattering method. Two LO and TO phonons for Li-P and Zn-P vibration modes were observed. LiZnP is constructed of the Li-P bond with the relatively high ionicity and the Zn-P bond with the relatively high covalency in the *same structure.*

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[20] See Chap. 9 in Ref. 13 for a detailed interpretation of the macroscopic transverse effective charge.

[21] Estimated to be the force constant $C = 4.44\times10^4$ (dyn/cm) for Li-P and $C = 6.54\times10^4$ (dyn/cm) for Zn-P using a simple expression $\omega_{\mathrm{TO}} = (C/\mu)^{1/2}$, where μ is the reduced mass.

[22] For example, see Table 9-1 in Ref. 13.