Electrical transport properties and crystal structure of LiZnAs

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The first report on the electrical transport properties of LiZnAs is presented. LiZnAs, which has an antifluorite structure, is a p-type semiconductor with energy band gap of about 1.1 eV. The intrinsic region is found at temperatures above 450 K. The typical resistivity, Hall mobility, and carrier concentration at room temperature are of the order of 10^{-1}–10 Ω cm, ≤ 30 cm^2/V sec, and 10^{17} cm^{-3}, respectively. For some crystals the disordered structure between Li and Zn sites is observed, accompanied by a dip in resistivity around 350 K.

The ternary compound LiZnAs has been characterized theoretically as a half ionic and half covalent tetrahedral semiconductor.[1] An electronic structure calculation[1] of LiZnAs revealed strongly covalent (Zn—As) and strongly ionic (Li—As) bonds in the same structure. Whereas the zinc-blende structure of a $D^{III}C^V$ compound (e.g., GaAs) has the D^{III} atom at $\tau_1 = (0,0,0)a$ (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_3, and τ_4 sites. Nowotny *et al.*[2] have reported the crystal structure of LiZnAs as follows: the τ_1, τ_2, and τ_3 sites are occupied by Zn, As, and Li atoms, respectively, while the τ_4 site is empty. This ternary compound belongs to the antifluorite structure.[3]

In this paper we report the first measurements of electrical transport properties of LiZnAs. We find that LiZnAs is a p-type semiconductor with energy band gap of about 1.1 eV and suggest the existence of a disordered structure between the Li and Zn sites.

The LiZnAs samples used in this study were prepared by direct reaction of equimolar amounts of Li (99.9% pure), Zn (99.999% pure), and As (99.999% pure). As reported earlier,[4] the successful crystal growth of the stoichiometric ratio was achieved by using 5 at. % excess Li and 3 at. % excess As to compensate for evaporation losses. A tantalum crucible was used as a container for the LiZnAs. The charged crucible was sealed under 10^{-4} Torr in a Pyrex tube. A vertical resistance furnace was heated up at a rate of 100 °C/h from 200 to 580 °C to promote crystallization. After holding for about 70 h, the furnace was cooled at a rate of 100 °C/h. The grown crystals were metallic gray 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 monophasic, exhibiting the antifluorite structure with $a = 5.940 \pm 0.001$ Å. This value is slightly larger than the value ($a = 5.924$ Å) reported by Nowotny *et al.*[2] Furthermore, the existence of disordered structure between the Li and Zn sites was found for some crystals by detailed x-ray diffraction intensity measurements, as discussed later. Differential
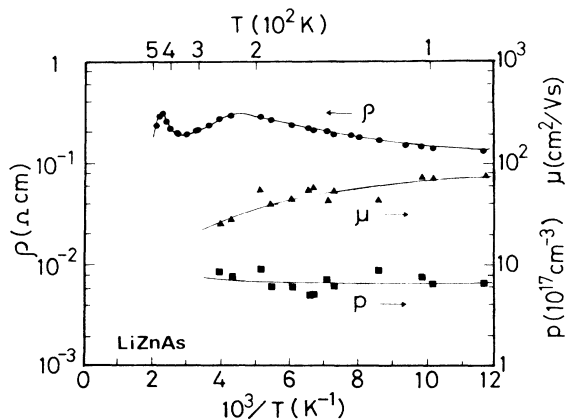

FIG. 1. The temperature dependence of the electrical properties (resistivity ρ, Hall mobility μ and hole concentration p) for LiZnAs (sample 3) with disordered structure.
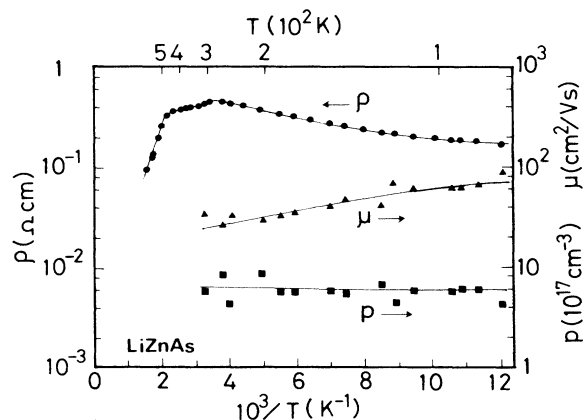
FIG. 2. The temperature dependence of the electrical properties (resistivity ρ, Hall mobility μ, and hole concentration p) for LiZnAs (sample 1) with ordered structure.

TABLE I. Typical experimental intensities (I_{expt}) and calculated intensities (I_{calc}) for ordered (sample 1) and disordered (sample 2) LiZnAs.

h	k	l	Ordered		Disordered	
			I_{expt}	I_{calc}	I_{expt}	I_{calc}
1	1	1	147	130	57	76
2	2	0	100	100	100	100
3	1	1	34	50	39	30
4	0	0	13	15	16	15
3	3	1	21	20	12	12
4	2	2	23	30	21	30

thermal analyses showed a broad endothermic peak around 850 °C, which we presume to indicate melting or decomposing of the LiZnAs crystal.

The electrical resistivity (ρ) and Hall coefficient (R_H) were measured by the Van der Pauw technique.[5] The samples used in these measurements were prepared by the same treatment used for the intermetallic compounds, LiAl (Ref. 6) and LiGa (Ref. 7). Tungsten probes were used as ohmic electrodes. The typical resistivity, Hall mobility ($\mu = R_H/\rho$), and carrier concentration ($p = 1/R_H e$) are shown in Figs. 1 and 2, respectively. All the crystals showed only p-type conductivity. This may originate from the lithium antisite defect (Li_{As}) in the arsenic sublattice of LiZnAs and this defect as well as the lithium antisite defect (Li_{Al}) in β-LiAl (Ref. 8) may cause the slight increase in lattice parameter. The resistivities of as-grown crystals were of the order of 10^{-1}–10 Ω cm at room temperature. The Hall mobility decreased monotonically from 80 to 30 cm²/V sec at ambient temperatures ranging from 77 to 300 K, whereas the hole concentration was almost constant at on the order of 10^{17} cm⁻³. However, an obvious difference in ρ was observed at temperatures ranging from 250 to 450 K, as shown in Figs. 1 and 2.

In order to clarify the cause of the difference in ρ, detailed x-ray diffraction analyses were carried out for each sample. As a result, we observed obvious differences in diffraction intensity between the (111) and (220) planes. The x-ray diffraction intensity was calculated assuming that LiZnAs has both the ordered and completely disordered structures between the Li and Zn sites. The structure factors of the ordered and disordered structures for Miller indices h,k,l odd are $(f_{Li}-f_{Zn})^2+f_{As}^2$ and f_{As}^2, respectively, whereas for $h+k+l=4n$ (h,k,l even) these are $(f_{Li}+f_{Zn}+f_{As})^2$ for both structures. Experimental intensities (I_{expt}) and calculated intensities (I_{calc}) for the ordered and disordered structures are listed in Table I. These results suggest the existence of disordered structure between Li and Zn sites. The samples with disordered structure have a dip in the resistivity around 350 K as shown in Fig. 1. Indeed, for cyclic resistivity measurements above room temperature the dip in the resistivity disappears corresponding to structural ordering with the variation of the resistivity, as shown in Fig. 3.

The forbidden band gap estimated from the slope of the intrinsic resistivity above 450 K using higher-resistivity samples was about 1.1 eV for both ordered and disordered structures, as shown in Fig. 4. At present, we cannot determine whether the optical gap of LiZnAs is direct or not since as-grown crystals are unstable in atmosphere.
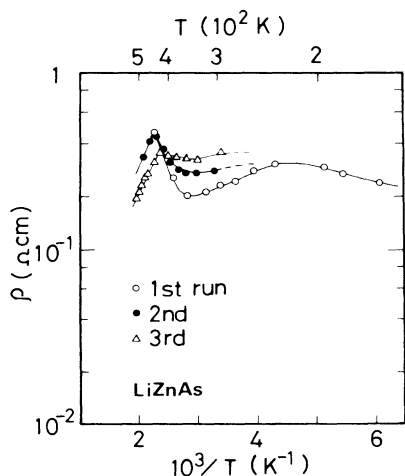

FIG. 3. The variation in electrical resistivity (ρ) for LiZnAs (sample 3) with disordered structure.

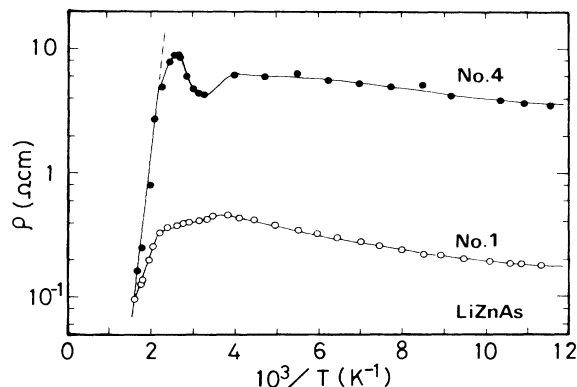

FIG. 4. The forbidden band gap estimated from the slope of the intrinsic resistivity (samples 1 and 4) above 450 K; $E_g \simeq 1.1$ eV.

In conclusion, we found that LiZnAs is a p-type semiconductor with energy band gap of about 1.1 eV, which was estimated from the intrinsic region above 450 K. The resistivity, Hall mobility, and carrier concentration at room temperature were 10^{-1}–10 Ω cm, ≤ 30 cm^2/V sec, and 10^{17} cm^{-3}, respectively. The disordered structure between Li and Zn sites was observed for some crystals accompanied by a dip in resistivity around 350 K.

[1]S. Wei and A. Zunger, Phys. Rev. Lett. **56**, 528 (1986).

[2]H. Mowotny and K. Bachmayer, Monatsch. Chem. **81**, 488 (1950).

[3]R. Juza, K. Langer, and K. Von Benda, Angew. Chem., Int. Ed. Eng. **7**, 360 (1968).

[4]K. Kuriyama and T. Kamijoh, J. Cryst. Growth **46**, 151 (1979).

[5]L. J. Van der Pauw, Philips Tech. Rev. **20**, 220 (1958).

[6]K. Kuriyama, T. Kamijoh, and T. Nozaki, Phys. Rev. B **22**, 470 (1980); K. Kuriyama, T. Nozaki, and T. Kamijoh, *ibid.* **26**, 2235 (1982).

[7]K. Kuriyama, K. J. Volin, T. O. Brun, and S. Susman, Phys. Rev. B **33**, 7291 (1986).

[8]K. Kishio and J. O. Brittain, J. Phys. Chem. Solids **40**, 933 (1979).