Electrical resistivity and electronic structure of the layered oxypnictides (LaO)ZnPn; Pn = P, As, Sb

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Abstract. We have synthesized the layered oxypnictides (LaO)ZnPn; Pn = P, As, Sb and investigated their electrical conductivity and the electronic structure. (LaO)ZnP and (LaO)ZnAs show typical semiconducting behaviors in the temperature dependence of the electrical resistivity. On the other hand, (LaO)ZnSb shows metallic behavior down to 150 K and semiconducting at lower temperature. Electronic structures were evaluated by photoemission spectroscopy. The possible valence band structure of each sample has been reported.

1. Introduction

At this late date, the layered oxypnictide (LaO)FeP as a new superconductor with transition temperature 4K, which have ZnCuSiAs type layered structure (P4/nmm), have been discovered[1], these layered systems have been extensively studied by many researchers and groups.

Our group has researched the layered oxychalcogenides (LaO)CuCh; Ch = chalcogen elements that has the same crystal structure as oxypnictides (LaO)TPn; T = transition metal elements, Pn = pnictogen, owing to transparency and luminescence with short wavelength. Recent years, one of these materials (LaO)CuS has been attracted as a transparent p-type semiconductor[2]. We have investigated the basic physical properties such as electrical resistivity, photoluminescence[3], photoemission spectroscopy[4], crystal structure, charge density distribution[5]. The valence band is found to be composed of Cu 3d (t₂g) - S 3p anti-bonding states, Cu 3d (e₃g) non-bonding states, and Cu 3d (t₂g) - S 3p bonding states from the photoemission studies. In this sample, the Cu₂S₂ layer seems to determine the physical properties.

Even oxychalcogenides and oxypnictides have the same ZnCuSiAs type structure, the physical properties are quite different each other. Especially, oxypnictides (LaO)TPn show various properties from semiconducting[6] or metallic to superconducting with depending on the transition elements. In this study, we dare focus on the Zn element as a transition metal element, which is expected to has no unoccupied state in the valence band, to investigate the effect of alteration from the divalent chalcogen
elements to the trivalent pnictogen elements on the physical properties, though most of general interests for this system seems to exist in understanding the superconductivity of (LaO)FeP and some related materials. The electrical resistivity and the electronic structure of the layered Zn oxypnictides (LaO)ZnP, (LaO)ZnAs, (LaO)ZnSb have been studied.

2. Experimental

All polycrystalline samples used in this study were prepared through solid-state reaction of La, La$_2$O$_3$, Zn, and pnictogen (P, As, Sb). The stoichiometric amount of these starting materials were mixed and then pressed into a rectangle under Ar atmosphere. The bar was sealed into an evacuated silica tube immediately and it was sintered at 950°C for 40 hours.

The powder X-ray diffraction (XRD) measurements were carried out at room temperature to characterize the crystallinity of the samples. The wavelength of X-ray was 1.5406 Å (Cu Kα line). The Bragg reflection data were collected from 20 to 60° in 2θ with a scan step of 0.01. Rietveld analysis was performed on the XRD profiles using the program code RIETAN2000[7], where the space group was assumed to be P4/nmm that is the same symmetry as oxychalcogenides (LaO)CuCh. The site-occupancy factors were set to the nominal value.

Electrical resistivity was measured from 300 K down to 10 K. For higher resistivity samples, a two-probe method was chose with high resistance bridge and a conventional four-probe method using for metallic samples.

Synchrotron photoemission spectroscopy (SPES) experiments were carried out on the beamline BL7 at Hiroshima Synchrotron Radiation Center. The synchrotron radiation from the storage ring was monochromatized by the Doragon-type monochromator. The photoemission spectra were measured using a hemispherical photoelectron analyzer (Gammadata Scienta SES100) with total energy resolution ~200 meV.

3. Results and Discussion

Figure 1 shows the XRD profiles of (LaO)ZnP, (LaO)ZnAs, (LaO)ZnSb with the simulation for (LaO)ZnSb calculated based on the space group P4/nmm. Though a few peak from impurity phases denoted by arrows are found, these samples seem to be almost single phase. All peaks shift toward lower 2θ with increasing atomic number, indicating lattice constants enlarge. The profile of (LaO)ZnSb is in good agreement of the simulated one. This indicates that the crystal structure of oxypnictides is the same as the oxychalcogenide’s one. Rietveld analysis shows that the lattice constants (a, c) of (LaO)ZnPn are (0.40405 nm, 0.8905 nm) for Pn = P, (0.40956 nm, 0.90690 nm) for As, and (0.42261 nm, 0.95378 nm) for Sb.

Figure 2 shows the temperature dependence of electrical resistivity. (LaO)ZnP has high value of the order of 10$^7$ Ω cm and a semiconducting behavior. (LaO)ZnAs indicates the same behavior with
smaller resistivity at room temperature than that of (LaO)ZnP. On the other hand, (LaO)ZnSb shows a metallic behavior, which is attributed to the spatial Sb 5p orbital, with relatively small resistivity of $10^9 \, \Omega \, \text{cm}$.

Figure 2. Temperature dependence of electrical resistivity

Figure 3 shows the SPES spectra of (LaO)CuS, (LaO)ZnSb, (c) schematic figure of valence band structure of (LaO)CuS, (d) proposed valence band structure of (LaO)ZnSb

Figure 3. SPES spectra and valence band structures: (a) SPES spectra of (LaO)CuS, (b) SPES spectra of (LaO)ZnSb, (c) schematic figure of valence band structure of (LaO)CuS, (d) proposed valence band structure of (LaO)ZnSb

The oxychalcogenide (LaO)CuS was also measured as a reference. We measured (LaO)ZnP and (LaO)ZnAs but their spectra have typical charged tendencies due to their high electrical resistivity. The SPES experiment will be retried to obtain the correct data.

Figure 3 shows the SPES spectra of (LaO)ZnSb and the schematic electronic structure. The oxysulfide (LaO)CuS that is in good agreement with our previous study [4] are mentioned. Each spectrum has mainly three structures denoted by A, B, C. With increasing the incident photon energy $\hbar \nu$, the
spectrum transforms but the three structures are remaining. The $h\nu$ dependence of the spectra are explained by the photoionization cross sections of the valence electron orbitals.[8] From these dependences, the valence band of (LaO)CuS consists of the Cu 3$d$, S 3$p$, and O 2$p$ states. In this crystal structure, one Cu ion is surrounded by four S ions tetrahedrally and this leads the splitting of the Cu 3$d$ states into the $t_{2g}$ and $e_g$ states. The $t_{2g}$ states in this symmetry well hybridize with the S 3$p$ states, while the $e_g$ states is almost localized. Therefore three structures A, B, C are attributed to the Cu 3$d$ ($t_{2g}$)–S 3$p$ anti-bonding states, Cu 3$d$ ($e_g$) non-bonding states and Cu 3$d$ ($t_{2g}$)–S 3$p$ bonding states, respectively. The obtained electron configuration is consistent with the first principle band calculation[].

Next, the spectra of (LaO)ZnSb is presented in Fig 4 (c). The SPES spectrum at $h\nu = 20$ eV has the structure D with low intensity and wide width, and the structure F with the structure E as a shoulder. At $h\nu = 30$ eV, the structure E is enhanced and the structure F almost disappears in the meantime the structure D has little change. In addition to these changes, the structure G newly appears. With widely increasing $h\nu$ to 100 eV, the structures D and F vanish. The structure E diminishes substantially and the structure G is, conversely, further enhanced. According to the photoionization cross section, the Sb 5$p$ orbital and the O 2$p$ orbital are dominant at 20 eV. When $h\nu$ increases to 30 eV, the Sb contribution to the spectrum rapidly decreases, in opposite, the O 2$p$ and the Zn 3$d$ contributions are growing up. At the highest $h\nu$, the main peak observed should be the Zn 3$d$ states and the small contribution from the O 2$p$ states exists. Hence the valence band consists of the Sb 5$p$, O 2$p$, and Zn 3$d$ states. In this case, the Zn 3$d$ states are almost localized without any hybridization, consequently, the top of the valence band seems to come from just the Sb 5$p$ states. This reveals that the metallic behavior of (LaO)ZnSb results from the outermost electrons of Sb.

4. Conclusions
We have studied the electrical resistivity and electronic structure of the layered oxypnictides (LaO)ZnPn; Pn = P, As, Sb. When choosing P or As as a pnictgen element, the samples are semiconductors, inversely the Sb sample is metallic. The valence band of (LaO)ZnSb, which is quite different from that of oxychalcogenides but has the same structure, is formed of the Sb 5$p$, O 2$p$, and Zn 3$d$ states. This crystal structure permits various combinations of elements coupling with the electronic structures. Namely, we can design the physical properties of this layered rare earth system from insulating or semiconducting to metallic without structure changes. The tolerance of this crystal structure provides us many functions such as superconductivity of (LaO)FeAs, good excitonic luminescence of (LaO)CuS.

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