Electronic Structures of Delafossite Cu(Al, M)O$_2$ and Thermoelectric Properties

Sunao Sugihara, Shunsuke Naitoh ,Takuya Kurotori and Hiroshi Maiwa
Department of Materials Science and Engineering, Shonan Institute of Technology,
1-1-25 Tsujido Nishikaigan, Fujisawa-shi 251-8511, Japan
Fax: 81-466-36-1594   e-mail: sugihara@mate.shonan-it.ac.jp

Delafossite oxide is popular for use as a conductive oxide that possesses a wide band gap. There are a few studies on thermoelectricity in relation to superlattices (layer-stuctured) and the substitution method. We study the delafossite CuAl$_{1-x}$M$_x$O$_2$ (M=Ni) for thermoelectricity. However, although the Seebeck coefficient shows a value of 450 μV/K, the thermoelectric properties are not good because of the high electrical resistivity and relatively higher thermal conductivity (30 W/mK). Our aim in this study is to improve the thermoelectric performance by replacing metal for the A or B site in the delafossite oxide. In our theoretical approach, we employed a molecular orbital method (DV-Xα method) to analyze the energy level structure, covalent bonding and density of states. The thermoelectric property may correspond to the calculation results. Here, we reported that electrical conductivity was improved when an impurity level appeared in the energy gap corresponding to CuAl$_{1-x}$M$_x$O$_2$, and Ni substitution was analyzed in terms of the spin state. We discuss the experimental results of the substitution on the basis of the first-principles calculations.

Key words: delafossite crystal, *ab initio* calculation, superlattice, energy level structure, density of states.

1. INTRODUCTION

The crystal CuAlO$_2$ is a wide band-gap material and a p-type semiconductor that is said to be difficult to dope. The optically measured direct band gap is 3.5 eV for CuAlO$_2$[1] and 3.9 eV[2]. Regarding thermoelectricity in delafossite materials, there have been few studies [3],[4]. In particularly, few have been performed on the three parameters Seebeck coefficient, electrical resistivity and thermal conductivity[5], which are discussed with the structure. That site-A substitution in ABO$_2$ employed Pt or Pd was discussed from the viewpoint of structure. The electronic structures were reported for a band calculation with the linear muffin tin orbital method [6], which was not discussed in thermoelectricity. The purpose of the study here is to analyze the electronic structures of CuAlO$_2$-based delafossite crystals, in relation to thermoelectricity. Here, the Al- site is substituted by Ni partially. The *ab initio* calculation is carried out using a cluster model with the molecular orbital method in considering of spin. We calculate energy level structures including energy gap, density of state for each up-and down-spin, bond order and effective charge.

2. CALCULATION METHODS

The first principles calculation is performed using DV-X α which is one of molecular orbital method to set a cluster, this being advantageous for bonding characteristics. The cluster model [Cu$_{12}$Al$_{21}$O$_{124}$]$^{-173}$

is illustrated in Fig. 1. For substitution by a metal, the centered- Al atom is replaced by the captioned elements, which are Cr, Fe, Ni, Zn, Ga, Ge, Mo, Ag, and In. The calculation results indicate energy gap, effective charge, bond overlap (covalent bonding) and partial density of states. On the other hand, we may compare the calculated electronic structures with the experimental results of thermoelectricity such as Seebeck coefficient, electrical resistivity and thermal conductivity.

3. RESULTS AND DISCUSSION

3.1 Energy gap

For the calculation of replacement by Ni, spin states are regarded and their energy gaps are listed with the original cluster Cu$_{12}$Al$_{21}$O$_{124}$ in Table 1. HOMO stands for the highest occupied molecular orbital and LUMO for lowest unoccupied molecular orbital. The energy gaps became less than their original values. The substituted atom is suggested to make an impurity level corresponding to an element. The lower electrical resistivity is expected due to the narrower gap with Ni-substitution, showing values of 0.24 and 1.16 eV for an up-spin and a down-spin, respectively.

3.2 Effective charge

When the value of effective charge (EC) is large, the ionicity of an element in the crystal should be stronger. The definition of EC is the difference in the number of

electrons between a normal charge and one after calculation. The fact that a small value of EC is obtained means that many electrons are being down away from the substituting metal.

3.3 X- ray photoelectron spectroscopy (XPS)

One method of securing of the *ab initio* calculation here is to make the main peak of the experimental spectra coincide with the calculated one, although there are no agreements from -2 eV down to approximately -8 eV as shown in Fig. 2. This method is often employed for the electrons around the Fermi level. The peaks around -5 eV are thought to be those of Cu 3d, but they were not clearly identified in the experimental data.

3.4 Covalent bond (CB)

Figure 3 shows the bond overlap population for each element with every metal-O, substituted metal-Al and -Cu bonding corresponding to the arrangement of elements in the crystal site. metal-O (place a) and metal-O (place b). A large bond overlap population indicates a large covalent bonding. It is the bonding of metal-O (place a) and metal-O (place b) that exhibits a large difference in the bonding strength corresponding to an element. Al, Ga and Ge show a larger value.

EC and CB do not seem to be clearly associated with thermoelectricity in terms of parameters such as Seebeck coefficient (α) and electrical resistivity (ρ); however, the balance between EC and CB in relation to electron transfer should be important for antinomy when measuring the two physical parameters α and ρ.

3.4 Partial density of states and energy gap

The partial density of states (PDOS) near the Fermi level provides informative spectra that indicate factors such as the change in electron density per unit energy and the energy gap between HOMO and LUMO. Basically, PDOS corresponds to the spectra of XPS as described above.

Figure 4 shows PDOS for every orbital in the standard CuAlO₂. The Cu 3d atomic orbital mostly appears at the Fermi level, and Cu 3d is split into valence and conduction bands with an energy gap of 3.05 eV. The PDOS for Ni -substitution is illustrated in Fig. 5, which shows up- and down-spin atomic orbitals after calculation, taking into consideration the spin states. There are two particular features in the Ni-substituted system: 1) Cu 3d and Ni 3d orbitals mostly occupy at Fermi level. 2) In the conduction level, Cu3d and O2p are hybridized. This calculation results suggest that the Ni-substituted system experimentally exhibits a low electrical resistivity.

Table 1 shows the energy gap in the case of transition-metal substitution in the standard CuAlO₂. As mentioned above, only in the Ni substitution system is the up-spin narrower than the down-spin and the energy level of LUMO relatively lower, such as 2.48 eV.

3.5 Discussion with experimental results

Here are some experimental results: in the standard system, the Seebeck coefficient was $850 \mu V \cdot K^{-1}$, ρ 1 Ω m and κ 31 $Wm^{-1}K^{-1}$ at 300 K[5]. On the other hand, Seebeck coefficient was $200 \mu V \cdot K^{-1}$, and ρ 2.7×10^{-3} Ω m and κ 13 $Wm^{-1}K^{-1}$ at 300K in the Ni-substituted

specimen (0.001 mol%). Thermal conductivity and electrical resistivity for the Ni-substituted delafossite were decreased significantly although Seebeck coefficient also decreased.

3.6 Thermoelectricity from electronic structures

First of all, Seebeck coefficient was calculated with a simple form; the Ni-substituted system has an energy gap of 0.24 eV in the up- spin state;

$$\alpha = \frac{k_B}{e} \frac{(E_F - E_i)}{k_B T} = 800 \ \mu V / K \quad , \text{--------(1)}$$

where E_F is the Fermi level, E_i impurity level, T=300 K and k_B and e follow the usual nomenclatures. The value of α approaches to the experimental one. Furthermore, the $3d^8 4s^2$ of the electron configuration of the Ni atom is $3d^9 s^1$ in crystal to result in two changes of state (g) associated with the Seebeck coefficient α ; g = 2 in this case, and

$$\alpha = (k_B / e) \ln g = 86.3 \quad (\mu \ V/K) \quad , \quad \text{----------(2)}$$

where is the Boltzman constant (J/K = V · C), and e is electronic charge (C). The calculated value in equation (2) is considered to be a component of the experimental value of Seebeck coefficient corresponding to the spin state when Al is substituted by Ni.

In considering electrical conductivity (or resistivity), the following Drude form explains it qualitatively;

$$\sigma = \frac{ne^2 \tau}{m^*} \quad , \quad \text{-------------------(3)}$$

where τ is the relaxation time, m* the effective mass, and n represents the number of electrons in the unit cell in the band (spin-up) which transverse E_F as described in the DOS of the Ni substitution system leading to better electrical conductivity. The denominator in the following equation (4)[8] represents the change in energy at E_F, which is large in the spin up state in Ni substitution system leading to a smaller m* than that of the original CuAlO. It also causes better electrical conductivity.

$$m^* = \frac{\hbar^2}{(d^2 E / dk^2)} \quad \text{------------------(4)}$$

Thermal conductivity must also be controlled to obtain a good thermoelectric material. However, it is difficult to find good way to improve electronic structures, although there have been some methods such as structural approaches or microstructures (layer, porosity, grain boundary), impurity addition and rattling compounds.

Here, we try to explain thermal conductivity in a microscopic approach in the ionic crystal. Most importantly, the vibration of the lattice can affect the transport of thermal energy in a way that makes it very

difficult to achieve an accurate theory of the thermal conductivity in the thermoelectric material. However, we suppose that the following equation describes electron-phonon coupling constant[9];

$$\left| g_{\mu\nu} \right|^2 = \frac{1}{V} \frac{4\pi e^2}{\left| k - k' \right|^2 + k_0} \times \frac{1}{2}\hbar\omega_{k-k'}$$

-------- (5)

where $g_{\mu\nu}$ is the electron-phonon coupling constant, k_0 the dielectric constant of oxide, and k and k' the wave vectors of an electron. The fact that the square of $g_{\mu\nu}$ vanishes linearly with the wave vector of the phonon has important consequences for the theory of the electrical resistivity[9]. This equation is also conjectured for thermal conductivity in a thermoelectric material. There is a case in which the kinetic energy of electrons will become negligible depending on temperature, although electrons themselves besides phonons take part in thermal conductivity. Accordingly, it is suggested by investigating electronic structures around the Fermi level that electron transfer ($k \rightarrow k'$) and screening by matrix oxide (related to dielectric constant) play an important role for thermal conductivity as microscopic images.

Furthermore, $\hbar\omega_{k-k'}$ represents phonon energy.

The Ni substitution system has a band hybridization between Cu3d and Ni3d, and it is suggested that a large difference in E_F level results in a large(k- k') in the denominator leading to small electron-phonon coupling, which is expected to result in low thermal conductivity.

4   SUMMARY

Electronic structures of the delfossite crystal $CuAlO_2$ were discussed with some experimental results (mostly for the Ni substitution system). We conclude that a large

Seebeck coefficient and a high electrical resistivity were elucidated by a large energy gap (3.05eV). Furthermore, electronic structures reflected to the electrical resistivity in the Ni- substitution system ($10^{-1} \Rightarrow 10^{-3} \Omega$ m). In consideration of thermal conductivity, it was suggested that it be reduced by controlling electron-phonon interaction, supposing energy level structures.

References
1） H.Kawazoe, M.Yasukawa, H.Hyoudo, M.Kurita, H.Yanagi and H.Hosono: Nature **389** (1997) 939-942.
2） H.Yanagi, S.Inoue, K.Ueda, H.Kawazoe, H.Hosono and H.Hamada: J. Appl. Phys, **88** (2000) 4159-4163.
3） X.Nie, S. Wei and S.B.Zhang: Phy. Rev. Lett. **88**, (2002) 066405-I—066405-4.
4） K.Koutomo, H.kozuka and W.S.Seo: Proceedings of 19th ICT (2000) 232-235.
5） T.Kurotori and S.Sugihara: Materials Transaction **46** (2005) 1462-1465.
6） H.Ueno, H.Okabe and M.Matoba: Proceedings of Thermoelectric Conference (TEC2001), 54-55, 2001.
7) K.Kobayashi and I.Terasaki, Proceedings of Thermoelectric Conference (TEC2002), 96-87, 2002.
8) C.Kittel, "Introduction to Solid State Physics", John Wiley & Sons, Inc., NY(1956) pp. 288-289.
9) N.W.Ashcroft and N.D.Mermin, "Solid State Physics", international edition, Saunders College Publishing, NY(1976) pp. 519-523.
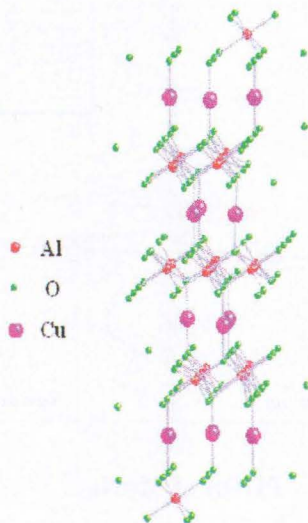
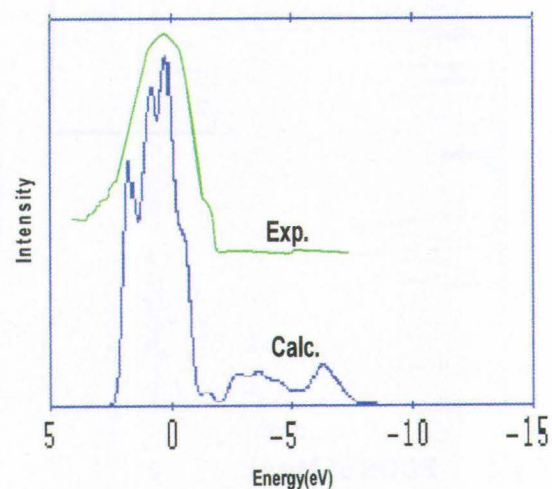**Fig.1 Cluster Model of [Cu12Al21O124]-173**

Fig.2 Calculation and Experiment

Table 1　Energy Gap for standard and Ni- substitution

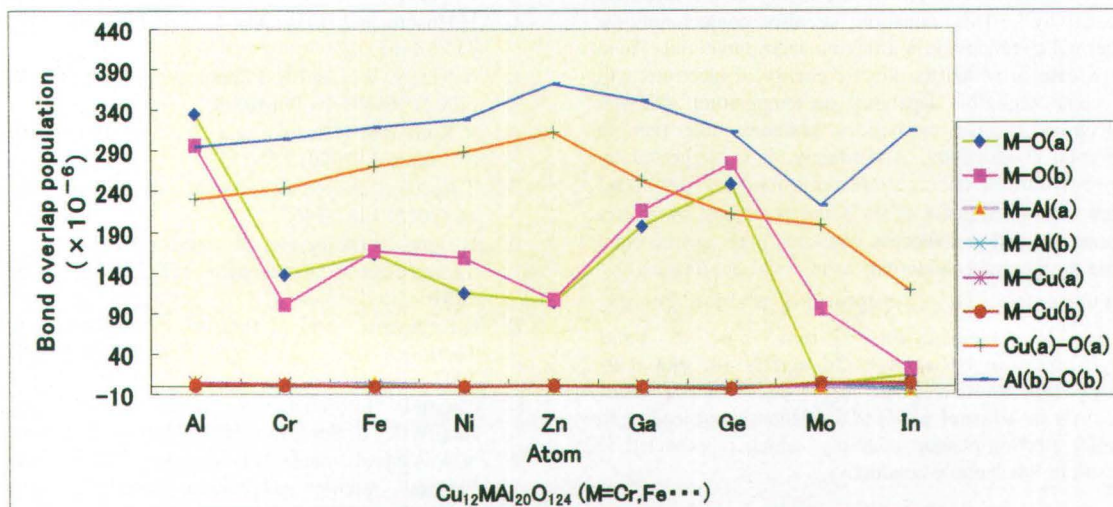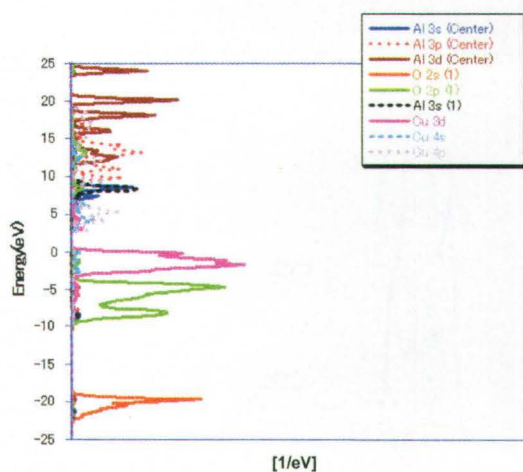|	Cluster model		HOMO (eV)	LUMO (eV)	Energy　gap (eV)
Standard (M=Al)	$Cu_{12}Al_{21}O_{124}$		1.91	4.96	3.05
M=Ni	$Cu_{12}NiAl_{20}O_{124}$	up	2.24	2.48	0.24
		down	1.77	2.93	1.16

Fig.3 Covalent bonding

Fig.4　PDOS of M=Al

Fig.5　PDOS of M=Ni