Transactions of the Materials Research Society of Japan 31[2] 387-389 (2006)

Thermoelectric Properties of Element-Substituted $CuAlO_2$

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The relationships between the thermoelectric properties (α, σ, κ) of element-substituted $CuAlO_2$ and the thickness of its layers (conducting layer and insulating layer) were investigated. The Al-O-Al angle of the insulating layer for depends on the a-axis, and the c-axis lattice parameter is related to the thickness of the conducting layer, which it consists of O-Cu-O structures. σ and κ are related to the thickness of the conducting layer. α is related to the insulating layer. However, above x=0.005, the thermoelectric properties are largely influenced by impurity.
Key words: delafossite, $CuAlO_2$, NiO, superlattice

1. INTRODUCTION

Delafossite, whose structure is shown in Fig.1, is given by the formula ABO_2 (A=Cu, Ag, Pt, Pd; B=Al, Ga, In, Cr, Fe, Co Y, La, etc.)[1]. Monovalent Cu or Ag (d^{10}) for A is a semiconductor; however, Pt or Pd (d^9) for A is known to show metallic conductivity [2][3]. This observation is elucidated by of s-d_z2 hybrid orbitals formed within the plane of A-ions. $CuAlO_2$ is known to be a p-type-conducting semiconductor. Its structure involves alternately stacking O-Cu-O and $Al^{3+}O_6$ structures the along c-axis. The Cu^+ ions are linearly coordinated by two O^{2-} ions to form a O-Cu-O dumbbell along the direction parallel to the c-axis, whereas, Al^{3+} ions are octahedral-coordinated by six O^{2-} ions [4][5]. The study focuses on the relationship between the thickness of the layer and the thermoelectric properties of element-substituted $CuAlO_2$. The possibility of realizing a high-efficiency thermoelectric conversion material that possesses a layer structure was reported [6][7]. In addition, various materials were reported [8-13]. It is of interest that the layer structure of $CuAlO_2$ exhibits a large thermopower. However, it has a very low electrical conductivity ($\sim 1\times10^2$ Sm^{-1} at 873K)[14][15]. If electrical conductivity can be improved, thermoelectric efficiency is expected to be high. However, reports on the thermoelectric properties of element-substituted $CuAlO_2$ have been few; in addition there has thus far been no report on thermal conductivity.

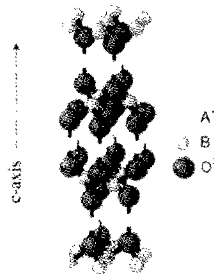

Fig.1 Crystal structure of delafossite-type ABO_2.

The purpose of this study is to determine the relationships between the thermoelectric properties of element-substituted $CuAlO_2$ and the thickness of its layers (thickness of conducting layer and insulating layer).

2.EXPERIMENTAL PROCEDURE

CuO, Al_2O_3 and NiO powders were used as raw materials for solid-state reaction. These materials were mixed in a molar ratio of Al_2O_3: NiO= (1-x): x (x=0, 0.001, 0.0025, 0.005 and 0.0075) a planetary ball mill for 2 h. The mixed powders were calcined at 1373 K for 12 h. Then, CuO was mixed with the calcined powder, ball-milled for 24 h, palletized, and calcined at 1373 K for 24 h. The sintered pellet was pulverized. Then, it was milled for 24 h. The mixture was pressed at 245 MPa and sintered at 1473 K for 48 h. Electrical conductivity and Seebeck coefficient were measured by the four-probe method, and thermal conductivity was measured by the laser flash method. Phase, crystal structures and lattice parameters were analyzed by X-ray diffraction (XRD) analysis.

3. RESULTS AND DISCUSSION

Figure 2 shows changing of a-axis and c-axis parameters for $CuAl_{1-x}Ni_xO_2$ samples lattice parameter for $CuAl_{1-x}Ni_xO_2$ samples. The a-axis drastically decreased at x=0.001 and in increased at x=0.0025; on the other hand, the c-axis increased at x=0.001 and decreased extremely at x=0.0025. The drastic decrease in the a-axis reduced Al-O-Al angle. Then, the angle makes the insulating layer thick; meanwhile, the increase in c-axis gives rise to the increase in the O-Cu-O distance of the conducting layer. Beyond x=0.001, an increase in the a-axis causes Al-O-Al angle leading to expand to the insulating layer becoming thin. Furthermore, the extreme decreasing of c-axis at x=0.0025 reduces the O-Cu-O distance of the conducting layer. According to XRD results, an impurity phase such as $NiAl_2O_4$ appeared at x=0.0075. From this

fact, it is suggested that the Ni system compound exists inside the conducting layer. If the Ni system compound is larger than the distance between layers of O-Cu-O, the a-axis increases, and the c-axis decreases. As a result, it is suggested that only the thickness the insulating layer decreases.

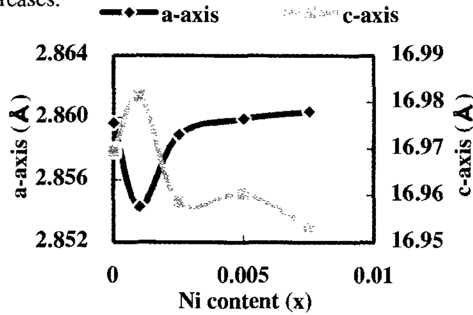

Fig.2 Changing of a-axis and c-axis parameters for $CuAl_{1-x}Ni_xO_2$ samples.

Figure.3 shows the relationship between lattice parameter and Seebeck coefficient (α) for $CuAl_{1-x}Ni_xO_2$ samples. (a) and (b) are α of RT and 850K, respectively. The α at RT decreases with increasing c-axis at x=0.001. It is suggested that the thickness of insulating layer is larger than thickness of conduction layer. α increases with decreasing c-axis at x=0.0025. Above x=0.0025, it decreases with decreasing c-axis. It is suggested that α decrease under the influence of the Ni system compounds impurity.

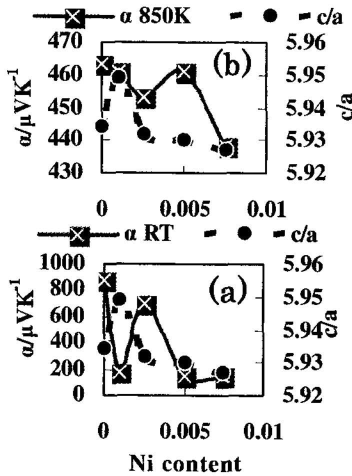

Fig.3 Relationship lattice parameter and α for $CuAl_{1-x}Ni_xO_2$ samples. (a) and (b) are α of RT and 850K, respectively.

Figure 4 shows the relationship between lattice parameter and electrical conductivity (σ) for $CuAl_{1-x}Ni_xO_2$ samples. (a) and (b) are σ of RT and 850K, respectively. σ shows a behavior similar to that of c-axis. Thus, it is a related to the in thickness of the conducting layer. Above x=0.005 at 850K, σ is larger than its value at x=0.0025. The increasing of σ at 850K is suggested to be attributable to the existence of Ni system compounds impurity.

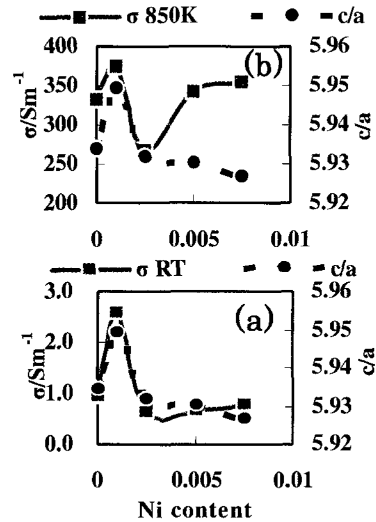

Fig.4 Relationship between lattice parameter and σ for $CuAl_{1-x}Ni_xO_2$ samples. (a) and (b) are σ of RT and 850K, respectively.

Figure 5 shows the relationship between lattice parameter and thermal conductivity (κ) for $CuAl_{1-x}Ni_xO_2$ samples. (a) and (b) are κ of RT and 850K, respectively. κ shows the same behavior as a-axis. Thus, it is related to the thickness of the conducting layer. Above x=0.0075 at 850K, the κ is larger than its value at x=0.005. The increasing of κ at 850K is suggested to be due to the influence of Ni system compounds impurity.

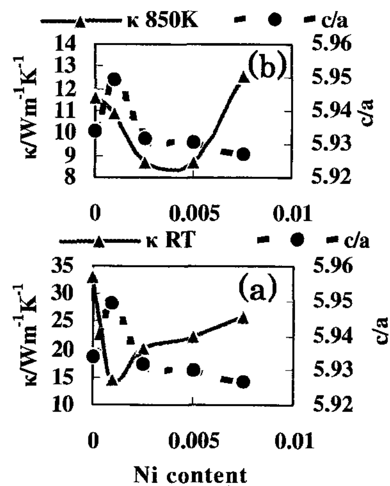

Fig.5 Relationship between lattice parameter and κ for $CuAl_{1-x}Ni_xO_2$ samples. (a) and (b) are κ of RT and 850K, respectively.

4. CONCLUSION

The relationships between layer structure and thermoelectric properties (α, σ, κ) were determined. a-axis parameter changes with the Al-O-Al angle of the insulating layer of, and c-axis parameter changes with the O-Cu-O length of the conducting layer. σ and κ are related to the conducting-layer thickness. α is related to the insulating-layer thickness. However, above x=0.005, thermoelectric properties become largely influenced by Ni compounds impurity.

5. REFERENCE

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(Received December 11, 2005; Accepted March 31, 2006)