Thermoelectric properties of delafossite-type layered oxides AgIn$_{1-x}$Sn$_x$O$_2$

Masahiro Yasukawa$^{a)}$ and Kaoru Ikeuchi  
Department of Materials Science and Engineering, Kochi National College of Technology, 200-1 Monobe, Nunokaki 783-8508, Japan  
Toshio Kono  
Kochi Prefectural Industrial Technology Center, 3992-3 Nunoshida, Kochi 781-5101, Japan  
Kazushige Ueda  
Department of Materials Science, Faculty of Engineering, Kyushu Institute of Technology, 1-1 Sensui, Tobata, Kitakyushu 804-8550, Japan  
Hideo Hosono  
Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori, Yokohama 226-8503, Japan  

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The thermoelectric properties of delafossite-type layered oxides AgIn$_{1-x}$Sn$_x$O$_2$ that consist of alternating layers of Ag and In$_{1-x}$Sn$_x$O$_2$ were investigated to elucidate their potential as a thermoelectric material. Polycrystalline materials of the AgIn$_{1-x}$Sn$_x$O$_2$ were prepared by a cation exchange reaction between NaIn$_{1-x}$Sn$_x$O$_2$ and AgCl. The solubility limit of the Sn atoms on the In sites was approximately $x=0.05$. The electrical conductivity and Seebeck coefficient were measured between 373 and 673 K in air. Undoped AgInO$_2$ was an $n$-type semiconductor with conductivities of $10^{-4}$–$10^{-2}$ Ω$^{-1}$ cm$^{-1}$, and the electron carriers were generated via the formation of oxygen vacancies. AgIn$_{0.95}$Sn$_{0.05}$O$_2$ was an $n$-type degenerate semiconductor with conductivities of $10^0$–$10^1$ Ω$^{-1}$ cm$^{-1}$ where the Sn atoms acted as electron donors. This drastic increase in the electrical conductivity increased the thermoelectric power factor by approximately two orders of magnitude to $10^{-6}$–$10^{-5}$ W m$^{-1}$ K$^{-2}$. © 2005 American Institute of Physics.

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I. INTRODUCTION

Thermoelectric energy conversion is an important technology for utilizing clean energy and development of thermoelectric materials with high efficiency of energy conversion is a key issue. Low-dimensional materials that consist of conducting one-dimensional (1D) chains or two-dimensional (2D) layers are promising for thermoelectric energy conversion. $^{1-4}$ One advantage of the low dimensionality proposed in these papers can be interpreted in terms of the carrier confinement effect in the conducting 1D chains or 2D layers, which leads to an enlarged absolute value of the Seebeck coefficient $S$ compared to the materials with three-dimensional conducting paths. Another advantage is a phonon-scattering effect due to the different chemical bonding between the chains or layers, which decreases the thermal conductivity $\kappa$. In addition, the electrical conductivity $\sigma$ of the low-dimensional materials can also be controlled by doping on the sublattice outside of the conducting paths to prevent the carrier mobility from decreasing. These three advantages are promising for a high thermoelectric figure of merit $Z$ expressed by the equation $Z=S^2\sigma/\kappa$, although there may be some trade-offs between the advantages.

Delafossite-type oxides are layered materials that consist of a variety of compositions expressed by the general formula $ABO_2$ ($A$=Pt, Pd, Cu, and Ag; $B$=Al, Ga, In, Sc, Cr, Fe, Co, Y, La, etc.). $^{5-7}$ The crystal structure consists of an alternating stacking of the $A^+$ layer and the ($BO_2)^-$ layer along the $c$ axis. There are two polytypes, rhombohedral (3$R$) and hexagonal (2$H$), according to the stacking sequence of a unit of the $A^+$ and ($BO_2)^-$ layers. $^{8}$ The 3$R$ type has a stacking sequence of $abc\bar{a}bc\cdots$, where each of $a$, $b$, and $c$ denotes a unit of the $A^+$ and ($BO_2)^-$ layers as shown in Fig. 1. The $A^+$ cations form linear O–A–O dumbbells parallel to the $c$ axis and the ($BO_2)^-$ layers form sheets with edge-sharing $BO_6$ octahedra. The O atom coordinated by one $A$ atom and three

$^a$Author to whom correspondence should be addressed; electronic mail: yasukawa@ms.kochi-ct.ac.jp

FIG. 1. Crystal structure of delafossite-type $ABO_2$ (space group: $R\bar{3}m$). The structure has a stacking sequence of $abc\bar{a}bc\cdots$ along the $c$ axis, where each of $a$, $b$, and $c$ denotes a unit of the $A^+$ and ($BO_2)^-$ layers. The solid line shows the trigonal unit cell.
B atoms has a sp$^3$-like bonding configuration. When the A$^+$ cation is monovalent Pt or Pd with a d$^9$ electronic configuration, the materials show a metallic conductivity, whereas the materials are semiconductors with monovalent Cu or Ag with d$^{10}$ closed shells. For the latter, transparent conducting thin films with both p-type and n-type conductivities are extensively developed based on the unique material design concept. Koumoto and co-workers reported the thermoelectric properties of several delafossite-type oxides, polycrystalline materials of PdCoO$_2$ and Ag$_2$O$_2$, and a single crystal of CuAlO$_2$ at high temperatures. They found that the PdCoO$_2$ and CuAlO$_2$ are promising thermoelectric materials that display a p-type conductivity.

We have selected a delafossite-type layered oxide AgInO$_2$ as a candidate of thermoelectric material. Transparent thin films of Sn-doped AgInO$_2$ with an n-type conductivity were fabricated by a rf-sputtering method and a pulsed laser deposition method. In these studies, the electrical conductivity was successfully controlled by Sn doping and the conducting paths for the electron carriers were considered to be In$_2$O$_3$ layers. In this study, polycrystalline bulk materials of AgIn$_{1-x}$Sn$_x$O$_2$ have been prepared by a cation exchange reaction and the thermoelectric properties have been investigated at high temperatures. The effect of Sn doping on the thermoelectric power factor is reported.

II. EXPERIMENT

Since it is known that the direct preparation of AgInO$_2$ delafossite by a conventional solid-state reaction of In$_2$O$_3$ with AgNO$_3$ or Ag$_2$O was unsuccessful, powder samples of delafossite-type AgIn$_{1-x}$Sn$_x$O$_2$ with $x=0.00$, 0.05, and 0.10 were prepared by a cation exchange reaction between NaIn$_{1-x}$Sn$_x$O$_2$ and AgCl. The starting materials, Na$_2$CO$_3$, In$_2$O$_3$, and SnO$_2$, were stoichiometrically weighed and mixed in ethanol. The mixed powder was pressed into a pellet, which was heated and intermittently ground at 1123 K for 20 h in air flow. The obtained NaIn$_{1-x}$Sn$_x$O$_2$ was ground and stoichiometrically mixed with AgCl in a mortar. The mixed powder was pressed into a pellet and the following cation exchange reaction was performed by heating at 673 K for 24 h in air with intermittent grinding:

NaIn$_{1-x}$Sn$_x$O$_2$ + AgCl $\rightarrow$ AgIn$_{1-x}$Sn$_x$O$_2$ + NaCl.

The pulverized sample was washed in distilled water, filtered, and dried at 353 K in air. Then the sample was pressed into a cylinder at 200 MPa using a cold isostatic press. Afterwards, it was heated at 673 K for 12 h in air. A phase identification was performed by x-ray-powder-diffraction (XRD) measurements using Cu Ka radiation (PANalytical, X’Pert). The electrical conductivity and Seebeck coefficient were measured at several temperatures between 373 and 673 K in air using an equipment developed in our laboratory. The electrical conductivity was measured by the direct current four-probe method. The Seebeck coefficient was evaluated by correcting the linear gradient of $\Delta V/\Delta T$ for the thermopower of platinum, where $\Delta V$ and $\Delta T$ are the thermoelectromotive force and the temperature difference between both ends of a sample measured by Pt leads and Pt/Pt–Rh thermocouples, respectively. Diffuse reflectance spectra were measured in a wavelength range of 200–2600 nm for the powder samples using double-beam spectrophotometer (Hitachi, U-4000). MgO powder was used as a reference. The Kubelka–Munk function spectra were obtained using the equation $f(R)=(1-R)^2/2R$, where $f(R)$ is the Kubelka–Munk function and $R$ is the diffuse reflectance.

III. RESULTS AND DISCUSSION

The XRD patterns for the samples with $x=0.00$ and 0.05 were indexed with a 3R-type delafossite structure of AgInO$_2$, indicating that the obtained samples with $x=0.00$ and 0.05 were single phases of the delafossite-type AgIn$_{1-x}$Sn$_x$O$_2$. The XRD pattern for the sample with $x=0.10$ showed a few weak diffraction peaks besides those arising from the 3R-type delafossite, which were due to AgCl and probably Sn-related oxide impurity. This result suggests that the solubility limit of the Sn atoms into the In site is approximately $x=0.05$ at the preparation stage of the precursor NaIn$_{1-x}$Sn$_x$O$_2$. Significant differences in the lattice parameters $a$ and $c$ of the 3R-type delafossite structure were not observed among the samples: $a=3.2764(2)$ Å, $c=18.875(3)$ Å for $x=0.00$, $a=3.2759(2)$ Å, $c=18.879(2)$ Å for $x=0.05$, and $a=3.2755(2)$ Å, $c=18.879(2)$ Å for $x=0.10$, respectively. These values are consistent with those previously reported for AgInO$_2$. Using the theoretical densities calculated from the lattice parameters, the estimated relative densities of the cylindrical samples were approximately 60%. Although the sample with $x=0.10$ included a small amount of impurities, the optical and thermoelectric measurements were performed for comparison.

Figure 2 shows the Kubelka–Munk function spectra. A
weak optical absorption starts at a photon energy of 2.05 eV
and a sharp increase in the absorption is observed at approxi-
mately 3 eV for all the samples. These two optical absorp-
tions correspond to the indirect and direct band gaps of the
delafossite-type AgIn$_{1-x}$Sn$_x$O$_2$, respectively.$^{13,18}$ Another op-
tical absorption is observed in the lower photon energy side
for the Sn-doped samples. This absorption is attributed to the
plasma oscillation of electron carriers generated from the
doped Sn atoms$^{13}$ and indicates that the doped Sn atoms act
effectively as electron donors.

Figure 3 shows the temperature dependence of the elec-
trical conductivity. The electrical conductivity for the un-
doped AgInO$_2$ is $10^{-4}$–$10^{-2}$ $\Omega^{-1}$ cm$^{-1}$ between 473 and
673 K, and the value increases as the temperature increases.
The 5-mol % Sn doping drastically enhanced the electrical
conductivity to $100$–$10^1$ $\Omega^{-1}$ cm$^{-1}$, which is more than three
orders of magnitude higher than that of undoped AgInO$_2$.
This enhanced electrical conductivity was also demonstrated
for 5-mol % Sn-doped AgInO$_2$ thin film.$^{12}$ Figure 4 shows
the temperature dependence of the Seebeck coefficient. The
signs of the Seebeck coefficient are negative for all the
samples, indicating that the materials are $n$-type conductors.
The absolute value of the Seebeck coefficient for the un-
doped AgInO$_2$ decreases with increasing temperature, sug-
cesting the increase in the electron carriers with the tempera-
ture increase. The absolute value of the Seebeck coefficient
dramatically decreases with 5-mol % Sn doping, corresponding
to the effective electron doping, but it remains higher than
$100 \mu$V K$^{-1}$ at 673 K.

The observed thermoelectric properties suggest that the
undoped AgInO$_2$ is an $n$-type semiconductor, and the elec-
tron carriers are probably generated from the oxygen vacan-
cies according to the following defect equilibrium using the
Kröger–Vink notation:

\[
O_2^- = V_0^- + 2e^- + 1/2O_2
\]

where $O_2^-$, $V_0^-$, and $e$ are the O$^{2-}$ anion in the delafossite
lattice, oxygen vacancy, and electron carrier, respectively, and
the superscripts $\cdot^-$, $^-$, and $^-$ denote effective charge states
of neutral, positive, and negative, respectively. It is likely
that the oxygen vacancy releasing two electrons as electron
donor increases as the temperature increases. For the Sn-
doped sample with $x=0.05$, the conductivity gradually in-
creases and the absolute value of the Seebeck coefficient
linearly increases as the temperature increases. These behav-
iors suggest that the AgIn$_{0.95}$Sn$_{0.05}$O$_2$ is a degenerate semi-
conductor and the Sn atoms doped in the delafossite lattice
act effectively as electron donors, being consistent with the
optical absorption by the electron carriers. There are no sig-
nificant differences in the electrical conductivity and See-
beck coefficient between the Sn-doped samples with $x=
0.05$ and 0.10. This is consistent with the XRD result that
the solubility limit of the Sn atoms into the In site is approxi-
mately $x=0.05$ and suggests that a small amount of impuri-
ties in the sample with $x=0.10$ hardly affect the thermoelec-
tric properties. Rogers et al.$^7$ explained the electrical
transport properties of the delafossite-type oxides using a
molecular-orbital energy diagram and the hybridization be-
tween $d_z^2$ and $s$ orbitals proposed by Orgel.$^{15}$ Their explana-
tion indicated that the valence band of the materials is com-
posed of filled $d_z^2$–$s$ hybrid orbitals or other nonhybrid $d$
orbitals that directly interact with the corresponding orbitals
of the neighboring Ag$^+$ cations in the $c$ plane due to the
relatively short distance between the Ag$^+$ cations [3.2772 Å
for AgInO$_2$ (Ref. 5)] and that the lower part of the conduc-
tion band is composed of empty antibonding orbitals be-
between the Ag $d_{z^2}$ and $s$ hybrid orbitals and the O $sp^3$ hybrid orbitals along the $c$ axis. For AgInO$_2$, the lowest part of the conduction band may be composed of antibonding orbitals between the In 5s and O $sp^3$ orbitals. Therefore, the electron carriers generated from the doped Sn atoms and the oxygen vacancies will move through the InO$_2$ layers, as described in the previous paper.$^{13}$ Figure 5 shows the temperature dependence of the thermoelectric power factor. The power factor values for undoped AgInO$_2$ are $10^{-8} - 10^{-7}$ W m$^{-1}$ K$^{-2}$ between 470 and 670 K, but 5-mol % Sn doping drastically enhanced the values to $10^{-6} - 10^{-5}$ W m$^{-1}$ K$^{-2}$ between 370 and 670 K. The power factor also increases with increasing temperature for all the samples. Since the relative densities of the present samples that had the electrical conductivity and Seebeck coefficient measured are still low ($\sim 60\%$), improving the relative density using an effective technique of ceramic processing or thin film preparation is considered the key to further increasing the electrical conductivity and, consequently, the power factor. Thus, AgIn$_{1-x}$Sn$_x$O$_2$ is a promising $n$-type thermoelectric material.

IV. CONCLUSIONS

Delafossite-type layered oxides AgIn$_{1-x}$Sn$_x$O$_2$ were prepared by a cation exchange reaction and the thermoelectric properties were investigated between 370 and 670 K.

(1) The solubility limit of the Sn atoms on the In sites is approximately $x=0.05$ in the present synthesis route.
(2) Undoped AgInO$_2$ is an $n$-type semiconductor in which electron carriers are generated via the formation of oxygen vacancies, whereas the Sn-doped material of AgIn$_{0.95}$Sn$_{0.05}$O$_2$ is an $n$-type degenerate semiconductor where the doped Sn atoms effectively act as electron donors.
(3) The optical absorption due to the electron carriers is clearly observed in the near-infrared wavelength region for the AgIn$_{0.95}$Sn$_{0.05}$O$_2$.
(4) The electrical conductivity is drastically enhanced with 5-mol % Sn doping and increases the thermoelectric power factor by approximately two orders of magnitude to $10^{-6} - 10^{-5}$ W m$^{-1}$ K$^{-2}$.

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