JOURNAL OF
Materials
CHEMISTRY
Communication

Thermoelectric properties of single crystal $CuAlO_2$ with a layered structure†

Kunihito Koumoto,* Hisashi Koduka and Won-Seon Seo

Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan. E-mail: g44233a@nucc.cc.nagoya-u.ac.jp

Received 22nd August 2000, Accepted 2nd October 2000
First published as an Advance Article on the web 20th November 2000

Delafossite-type $CuAlO_2$ has been found to be promising for thermoelectric conversion.

Thermoelectric materials with high energy conversion efficiency are strongly required for the future technology of heat recovery and its effective utilization, and for refrigeration of electronic devices. A variety of new concepts and new materials for this purpose have been proposed in the past ten years. One of the most exiting proposals was superlattice quantum-well materials.[1–4] Theoretical evidence that a superlattice (2D and 1D) would enhance the thermoelectric figure-of-merit, Z ($=\sigma\alpha^2/\kappa$, where σ is the electrical conductivity, α is the Seebeck coefficient, and κ is the thermal conductivity), has triggered extensive experimental investigations.[5] Even though the effectiveness of a superlattice structure has been partially verified by experiments, manufacturing actual materials with the expected properties has also been recognized to be difficult.

Crystals having layered structures or chain structures can be regarded as natural superlattices. They exist as thermodynamically stable phases, so that it is usually easy and of low cost, compared with artificial superlattices, to synthesize them. Among oxide materials which have been actively investigated in recent years, those possessing layered structures, such as $NaCo_2O_4$ (p-type)[6] and $(ZnO)_mIn_2O_3$ (n-type),[7–9] show fairly high figures-of-merit. The reason for this finding is still unclear, but it should be associated with the correlation between the low dimensionality of a crystal structure and the behavior of electrons and phonons in an anisotropic structural environment.

In the present study, we focused our attention on $CuAlO_2$ possessing a natural superlattice (layered) structure. $CuAlO_2$ crystallizes in the delafossite ($CuFeO_2$; space group $= R\bar{3}m$) structure.[10] In a large number of compositions, ABO_2 (A = Cu, Ag, Pt, Pd; B = Al, Ga, In, Cr, Fe, Co, Y, La, *etc.*), possessing the delafossite structure, those with monovalent Cu or Ag (d^{10}) for A are semiconductors and those with monovalent Pt or Pd (d^9) are known to show metallic conductivity.[11–13] This phenomenon has been explained by means of s–d_{z^2} hybrid orbitals formed within the plane of A ions,[14] and this model has recently been proved to be qualitatively correct by band-structure calculations.[15] Polycrystals or thin films of $CuAlO_2$ are known to show p-type semiconductivity,[16,17] but thermoelectric properties have never been reported in the literature so far. Here, we first report the anisotropic electrical conductivity of a single crystal and propose that $CuAlO_2$ should become a candidate thermoelectric material.

Single crystal growth was carried out according to the method reported by Ishiguro *et al.*[18] Firstly, polycrystals were synthesized through solid state reactions between Cu_2O and Al_2O_3, and secondly single crystals were grown by a flux method. Powders of CuO and Al_2O_3 were weighed in 2 : 1 proportion (molar ratio), mixed in a ball mill for 24 h, and further fired at 1200 °C for 12 h in air. The sintered compact was composed of $CuAlO_2$ polycrystals as confirmed by X-ray diffraction analysis. They were crushed in an alumina mortar and mixed with CuO powder employed as a flux agent in $CuAlO_2 : CuO = 1 : 15$ molar ratio. The mixture was placed in a platinum boat instead of an alumina boat, as was employed by Ishiguro *et al.* Since the growing crystal contains alumina as a major component, we avoided using an alumina boat to prevent any reaction between the container and reactants from occurring. The mixture was heated at the rate of 10 °C min^{-1} up to 1200 °C, kept for 5 h, then slowly cooled at the rate of 0.5 °C h^{-1} down to 1050 °C in an electric furnace, the temperature of which could be precisely controlled. After cooling to room temperature, the CuO flux was removed by rinsing with a 1 M HNO_3 solution.

Synthesized crystals were characterized using a powder X-ray diffractometer, a transmission electron microscope and an electron-probe microanalyzer. Single crystallinity was also examined by taking Laue photographs for a few pieces of crystals. Most of the crystals grown were small and in a plate form with the *c*-axis perpendicular to the plate surface, so that electrical conductivity along the *ab*-plane (perpendicular to the *c*-axis) was measured by the usual van der Pauw method, while the electrical conductivity along the *c*-axis was measured by a dc four-probe method. Platinum was employed for electrodes. The Seebeck coefficient along the *ab*-plane could be measured

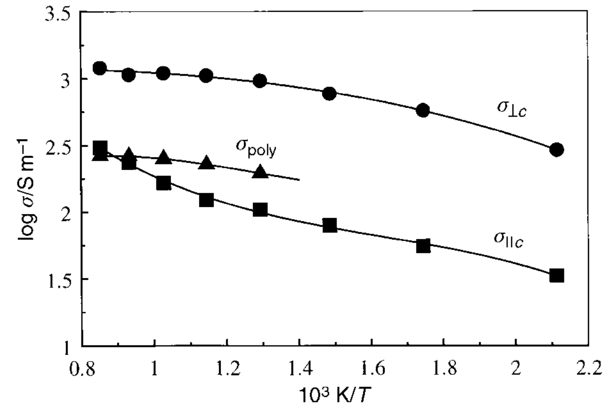

Fig. 1 Electrical conductivity *vs.* temperature for a single crystal measured along the *ab*-plane ($\sigma_{\perp c}$) and the *c*-axis ($\sigma_{\parallel c}$). The conductivity of a polycrystal (σ_{poly}) is shown for comparison.

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†Electronic supplementary information (ESI) available: crystal structure of delafossite-type ABO_2; SEM image, XRD patterns, ED and HRTEM images of a $CuAlO_2$ single crystal. See http://www.rsc.org/suppdata/jm/b0/b006850k/

DOI: 10.1039/b006850k

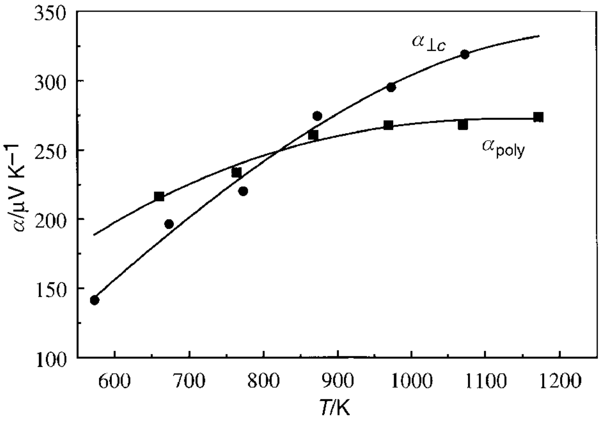

Fig. 2 Seebeck coefficient *vs.* temperature for a single crystal measured along the *ab*-plane ($\alpha_{\perp c}$). The Seebeck coefficient of a polycrystal (α_{poly}) is shown for comparison.

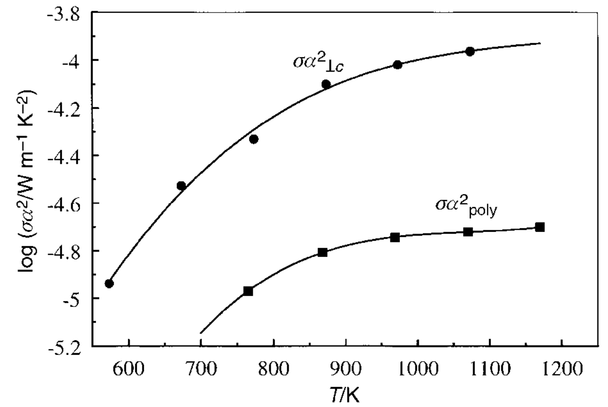

Fig. 3 Thermoelectric power factor *vs.* temperature for a single crystal ($\sigma\alpha^2_{\perp c}$) and a polycrystal ($\sigma\alpha^2_{\text{poly}}$).

using thin Pt–Pt/Rh thermocouples, but that along the *c*-axis could not be measured because the crystals were too thin to generate a measurable temperature difference.

The single crystals obtained were very small in size, and the largest one was only $2 \times 3 \times 0.2$ mm^3. They were usually lustrous black and had a hexagonal plate-like shape, and the metal composition, Cu : Al, was confirmed to be approximately unity (actually 50.3 : 49.7) by electron-probe microanalysis. Some of thin crystals were found to be translucent. X-Ray diffraction measurement has demonstrated that the *ab*-plane of the hexagonal unit cell is parallel to the surface of a platy crystal, and X-ray Laue measurement has shown that these crystals are monocrystalline, and a high-resolution transmission electron micrograph (HRTEM) clearly demonstrated that the crystal had a two-dimensional layer structure.

Electrical conductivity along the *ab*-plane ($\sigma_{\perp c}$) and *c*-axis ($\sigma_{\parallel c}$) both increased with increasing temperature (Fig. 1), and the Seebeck coefficient was always positive as shown in Fig. 2 indicating that $CuAlO_2$ is a p-type semiconductor. p-Type semiconduction must take place owing to the deviation from the stoichiometric composition induced according to the following defect equilibrium, though the exact nonstoichiometry is not known yet:

$$O_2(g) = 2O_o^x + V_{Cu}' + V_{Al}''' + 4h^{\cdot} \qquad (1)$$

where O_o, V_{Cu}, V_{Al}, and h denote lattice oxygen, Cu vacancy, Al vacancy, and electron hole, respectively, and the superscripts ^{x}, $'$, and $\cdot$ denote effective charge states indicating neutral, negative, and positive, respectively. Electron holes correspond to divalent copper ions, Cu^{2+}, and they would move in a valence band for conduction.

Band structure calculations have exhibited that the valence band is dominated by the Cu 3d states and the Cu 4s states show only a small contribution, while the lower part of the conduction band is dominated by the Cu 4s states.[15] This band picture is in good agreement with the Orgel model that proposed an s–d_{z^2} hybridization with the Cu–O bonds along the *z*-axis for linearly coordinated Cu^+ ions.[14] The band structure would firmly indicate that the Cu layers (two-dimensional hexagonal packing of Cu^+ ions) would behave as conduction paths for carriers (holes). Fig. 1 clearly shows that $\sigma_{\perp c}$ is actually about an order of magnitude higher than $\sigma_{\parallel c}$, and carriers are easier to move two-dimensionally along the *ab*-plane than to move across the Al–O insulating layers. This result supports our suggestion that $CuAlO_2$ can be regarded as having a superlattice structure where charge carriers can be effectively confined in the Cu layers.

The Seebeck coefficient (α) along the *ab*-plane shows a larger temperature dependence than that of polycrystalline ceramics (Fig. 2). Although it could not be measured, α along the *c*-axis may show a smaller temperature dependence. The power factor, $\sigma\alpha^2$, along the *ab*-plane is quite large compared to that of a polycrystal as shown in Fig. 3, and this observation strongly suggests the two-dimensionality of a crystal structure. The power factor itself along the *ab*-plane is rather large compared to other oxide materials, and $CuAlO_2$ may become a candidate material for thermoelectric energy conversion. Practical materials should be crystal-plane (*ab*-plane) oriented ceramics to which a temperature difference is applied along the *ab*-plane for thermoelectric power generation.

Acknowledgements

We are grateful to Dr W. Pitschke of IFW Dresden for his assistance in taking Laue photographs and to Professor I. Terasaki of Waseda University for his advice in electrical conductivity measurements.

Notes and references

1 L. D. Hicks and M. S. Dresselhaus, *Phys. Rev. B*, 1993, **47**, 12727; L. D. Hicks and M. S. Dresselhaus, *Phys. Rev. B*, 1993, **47**, 16631.
2 L. D. Hicks, T. C. Harman and M. S. Dresselhaus, *Appl. Phys. Lett.*, 1993, **63**, 3230.
3 P. J. Lin-Chung and T. L. Reinecke, *Phys. Rev. B*, 1995, **51**, 13244.
4 D. A. Broido and T. L. Reinecke, *Phys. Rev. B*, 1995, **51**, 13797.
5 M. S. Dresselhaus, T. Koga, X. Sun, S. B. Cronin, K. L. Wang and G. Chen, *Proc. 16th Int. Conf. on Thermoelec.*, ed. A. Heinrich and J. Schumann, IEEE, Dresden, 1997, pp. 12–20.
6 I. Terasaki, Y. Sasago and K. Uchinokura, *Phys. Rev. B*, 1997, **56**, 12685.
7 H. Ohta, W. S. Seo and K. Koumoto, *J. Am. Ceram. Soc.*, 1996, **79**, 2193.
8 M. Kazeoka, H. Hiramatsu, W. S. Seo and K. Koumoto, *J. Mater. Res.*, 1998, **13**, 523.
9 Y. Masuda, M. Ohta, W. Pitschke, W. S. Seo and K. Koumoto, *J. Solid State Chem.*, 2000, **150**, 221.
10 W. Soller and A. J. Thompson, *Phys. Rev.*, 1935, **47**, 664.
11 R. D. Shannon, D. B. Rogers and C. T. Prewitt, *Inorg. Chem.*, 1971, **10**, 713.
12 C. T. Prewitt, R. D. Shannon and D. B. Rogers, *Inorg. Chem.*, 1971, **10**, 719.
13 D. B. Rogers, R. D. Shannon, C. T. Prewitt and J. L. Gillson, *Inorg. Chem.*, 1971, **10**, 723.
14 L. E. Orgel, *J. Chem. Phys.*, 1958, 4186.
15 A. Buljan, P. Alemany and E. Ruiz, *J. Phys. Chem. B*, 1999, **103**, 8060.
16 F. A. Benko and F. P. Koffyberg, *J. Phys. Chem. Solids*, 1984, **45**, 57.
17 H. Kawazoe, M. Yasukawa, H. Hyodo, M. Kurita, H. Yanagi and H. Hosono, *Nature*, 1997, **389**, 939.
18 T. Ishiguro, N. Ishizawa, N. Mizutani and M. Kato, *J. Solid State Chem.*, 1981, **40**, 170.