

九州工業大学学術機関リポジトリ



Title	Thermoelectric properties of layered oxyselenides $\text{La}_{1-x}\text{Sr}_x\text{CuOSe}$ ($x = 0$ to 0.2)
Author(s)	Yasukawa, Masahiro; Ueda, Kazushige; Hosono, Hideo
Issue Date	2004-04-01
URL	http://hdl.handle.net/10228/574
Rights	Copyright © 2004 American Institute of Physics

Thermoelectric properties of layered oxyselenides $\text{La}_{1-x}\text{Sr}_x\text{CuOSe}$ ($x=0$ to 0.2)

Masahiro Yasukawa^{a)}

Department of Materials Science and Engineering, Kochi National College of Technology, 200-1 Monobe, Nankoku 783-8508, 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

(Received 16 September 2003; accepted 17 December 2003)

Thermoelectric properties of layered oxyselenides $\text{La}_{1-x}\text{Sr}_x\text{CuOSe}$ ($x=0.00$ to 0.20) were investigated to evaluate the potential as thermoelectric material. Temperature dependence of the electrical conductivity and Seebeck coefficient measured in a temperature range of 373 to 673 K indicated that nondoped LaCuOSe was a p -type degenerate semiconductor due to Cu vacancies, while Sr-doped materials with $x=0.05$ to 0.20 were p -type metals. The electrical conductivity increased and Seebeck coefficient decreased with increasing Sr concentration up to $x=0.10$ in $\text{La}_{1-x}\text{Sr}_x\text{CuOSe}$, suggesting that the effective hole carriers increase with increasing Sr content up to $x=0.10$. Thermoelectric power factors were drastically enhanced by the Sr doping, and the value reached $1.0\text{--}1.4 \times 10^{-4} \text{ W m}^{-1} \text{ K}^{-2}$ for $\text{La}_{0.95}\text{Sr}_{0.05}\text{CuOSe}$. Thermal conductivities measured for the materials with $x=0.00$ and 0.05 were $2.1 \text{ W m}^{-1} \text{ K}^{-1}$ and $2.3 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature, respectively. These results lead to an estimation of Z value of $4.4 \times 10^{-5} \text{ K}^{-1}$ for $\text{La}_{0.95}\text{Sr}_{0.05}\text{CuOSe}$.

© 2004 American Institute of Physics. [DOI: 10.1063/1.1646438]

I. INTRODUCTION

Oxychalcogenides expressed by a general formula, LnCuOCh (Ln: trivalent rare-earth ions, Ch: chalcogenide ions such as S, Se, and Te), are known to crystallize in the same layered structure.¹ There are several variations in the layered oxychalcogenides according to combinations of the constituent elements.¹⁻³ The crystal structure of a prototype material, LaCuOSe , is schematically pictured in Fig. 1. The crystal structure consists of an alternate stack of the LaO layer and the CuSe layer along the c axis. The LaO and CuSe layers are considered to be insulating and conducting layers, respectively. As conjectured from the energy band structure calculated for LaCuOS ,⁴ the valence band of LaCuOSe is composed of $\text{Cu } 3d\text{--} \text{Se } 4p$ antibonding states, so that the hole carriers are doped into the CuSe layers via Sr doping for La or formation of Cu vacancies. A metal-insulator transition was reported for Sr-doped LaCuOS and LaCuOSe , demonstrating that the electrical conductivity increased to values higher than $10 \Omega^{-1} \text{ cm}^{-1}$ with Sr doping for LaCuOS (Ref. 5) and LaCuOSe .⁶ In addition, wide-gap and exciton emission properties were found in $\text{LaCuOS}_{1-x}\text{Se}_x$.⁷ These optical and electrical properties give promise to the layered oxychalcogenides as functional materials.

We consider that a thermoelectric converter is one of the applications of the layered oxyselenides because their crystal

and electronic structures seem to have advantages for thermoelectric applications. (1) The CuSe layer consists of two-dimensional (2-D) network of edge-sharing CuSe_4 tetrahedra and is regarded as 2-D sublattice of Cu_2Se , which is known as a thermoelectric material.⁸ The absolute value of Seebeck coefficient (S) for LaCuOSe is expected to be larger than that for the three-dimensional Cu_2Se due to the carrier confinement effect in the CuSe layers.⁹ (2) Phonon scattering in the c -axis direction is considered to be large because chemical bonding is very different among La-O , La-Se , and Cu-Se . The large phonon scattering will decrease the thermal conductivity (κ) of LaCuOSe . (3) This material can show metallic behavior with high electrical conductivity (σ), and the carrier concentration in the conducting layer is controllable by ion substitution in the insulating layer. These three factors are promising for high thermoelectric figure of merit Z expressed by an equation $Z=S^2\sigma/\kappa$, although there may be some trade-off between the factors. Thermoelectric properties of LnCuOS oxysulfides have been already reported by Ishikawa *et al.*,¹⁰ but those of the oxyselenides have not yet been reported. In this study, we have selected the layered oxyselenide LaCuOSe as a candidate thermoelectric material, and the thermoelectric properties of Sr-doped LaCuOSe and the effect of Sr doping are reported.

II. EXPERIMENT

Sintered samples of $\text{La}_{1-x}\text{Sr}_x\text{CuOSe}$ with $x=0.00, 0.05, 0.10, 0.15,$ and 0.20 were prepared from starting materials of

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

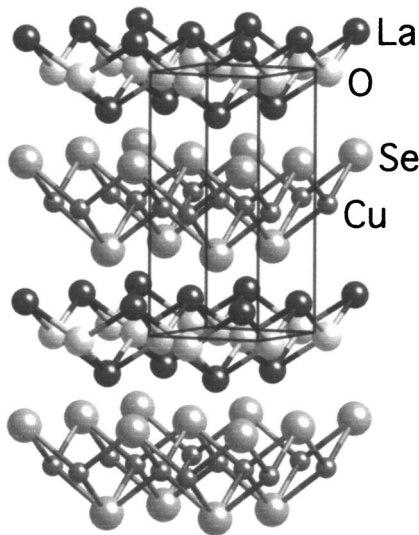


FIG. 1. Crystal structure of LaCuOSe. PbO-type LaO layer and anti-PbO-type CuSe layer are alternately stacked along the *c* axis. Solid line shows the tetragonal unit cell.

La₂O₃, La₂Se₃, SrO, Cu, and Se powders. These powders were stoichiometrically weighed in Ar atmosphere and sealed in an evacuated silica tube. The powders were then mixed and heated at 1073 K for 6 h. The obtained powders were pulverized and molded in a graphite die, and sintered at 1073 K for 5 min under vacuum by spark plasma sintering. X-ray powder diffraction (XRD) patterns were measured at room temperature using Cu K_α radiation. Electrical conductivity and Seebeck coefficient were measured at several temperatures in a temperature range of 373 to 673 K in N₂ gas flow. The electrical conductivity was measured by a dc four-probe method. The Seebeck coefficient was evaluated by correcting the linear gradient of $\Delta V/\Delta T$ for thermopower of platinum,¹¹ where ΔV and ΔT are the thermoelectromotive force and temperature difference between both ends of a sample measured by Pt leads and Pt/Pt-Rh thermocouples, respectively. Thermal conductivity was estimated at room temperature for the samples with $x=0.00$ and 0.05 as a product of the bulk density, thermal diffusivity, and specific heat. The latter two parameters were measured by the laser flash method.

III. RESULTS AND DISCUSSION

A powdered sample of the sintered LaCuOSe ($x=0.00$) was brown, while the Sr-doped samples with $x=0.05$ to 0.20 showed dark brown color. All the XRD patterns for the sintered samples with $x=0.00$ to 0.20 were indexed with tetragonal symmetry assuming the space group of $P4/nmm$, and no impurity phase was observed. Therefore, all the sintered samples were single phase of the layered oxy-selenide, and the La sites were replaced with the Sr atoms up to $x=0.20$ in the La_{1-x}Sr_xCuOSe. There was no significant difference in the lattice constants *a* and *c* among the samples: $a \sim 4.07$ Å and $c \sim 8.80$ Å, in good agreement with those previously reported for LaCuOSe.¹² This is probably due to almost equal ionic radii between La³⁺ and Sr²⁺ ions.¹³ The relative densities of the sintered samples were

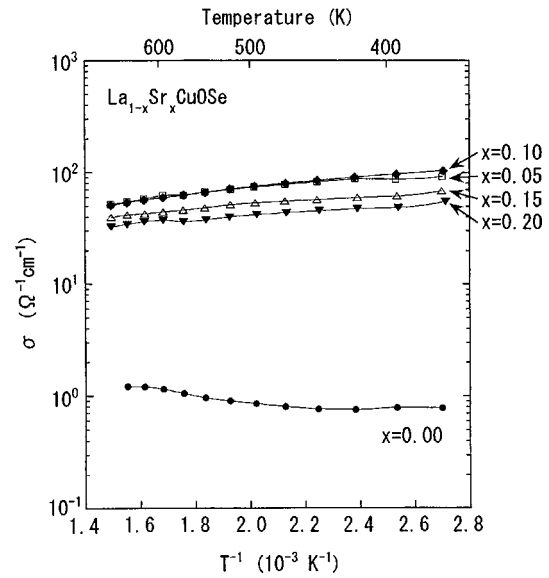


FIG. 2. Temperature dependence of the electrical conductivity σ for the La_{1-x}Sr_xCuOSe ($x=0.00$ to 0.20). The electrical conductivity was measured in the temperature range of 373 to 673 K in N₂ gas flow.

estimated to be 84%, 96%, 93%, 90%, and 95% for $x=0.00, 0.05, 0.10, 0.15,$ and 0.20 , respectively.

Temperature dependence of the electrical conductivity and Seebeck coefficient is shown in Figs. 2 and 3, respectively. The signs of the Seebeck coefficient were positive for all the samples, indicating that the materials were *p*-type conductors. The electrical conductivities for the sample with $x=0.00$ were $\sim 1 \Omega^{-1}\text{cm}^{-1}$ in the measured temperature range, and the value increased gradually with increasing temperature. The Seebeck coefficient for the sample with $x=0.00$ increased with increasing temperature. These properties suggest that the nondoped sample is a *p*-type degenerate semiconductor. The origin of the hole carriers is probably acceptors derived from the Cu vacancies, which were formed unintentionally during the synthesis. The degenerate behav-

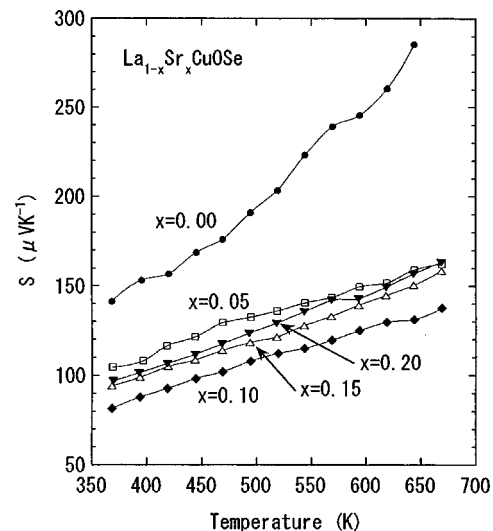


FIG. 3. Temperature dependence of the Seebeck coefficient S for the La_{1-x}Sr_xCuOSe ($x=0.00$ to 0.20). The Seebeck coefficient was measured in the temperature range of 373 to 673 K in N₂ gas flow.

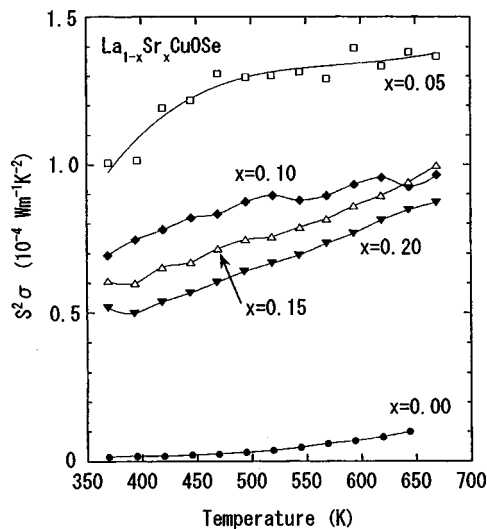


FIG. 4. Temperature dependence of the thermoelectric power factor $S^2\sigma$ for the $\text{La}_{1-x}\text{Sr}_x\text{CuOSe}$ ($x=0.00$ to 0.20).

ior suggests that the acceptor levels are very close to the valence band maximum composed of $\text{Cu } 3d - \text{Se } 4p$ antibonding states. With the Sr doping of $x=0.05$ to 0.20 , the electrical conductivity increased drastically to values ranging from 30 to $100 \text{ } \Omega^{-1} \text{ cm}^{-1}$, and the conductivity for the Sr-doped samples decreased with increasing temperature. The Seebeck coefficients for the Sr-doped samples became much smaller than those of the nondoped sample, and the values increased linearly with increasing temperature. These phenomena indicate that all the Sr-doped samples show metallic behavior with p -type electrical conductivity. The electrical conductivity was maximized for the samples with $x=0.05$ and 0.10 , and it decreased gradually with increasing x for $x \geq 0.10$. The Seebeck coefficient decreased upon increasing x from $x=0.00$ to $x=0.10$, while it increased slightly for $x \geq 0.10$. These results suggest that the effective hole carriers are continuously introduced into the valence band, that is, CuSe layers with increasing Sr concentration until $x=0.10$. The decrease in the electrical conductivity and the increase in the Seebeck coefficient observed for $x \geq 0.15$ may be due to a mechanism such as carrier compensation or enlargement of effective mass of hole carriers in the heavily doped materials, although it is not clear at present.

Temperature dependence of the thermoelectric power factor $S^2\sigma$ is shown in Fig. 4. The power factors for the sample with $x=0.00$ were lower than $10^{-5} \text{ W m}^{-1} \text{ K}^{-2}$. The power factor was drastically enhanced by the Sr doping and maximized to values of $1.0 - 1.4 \times 10^{-4} \text{ W m}^{-1} \text{ K}^{-2}$ for $x=0.05$. The values for the samples with $x \geq 0.05$ decreased continuously with increasing x . Although we found the maximum of the power factor at $x=0.05$, the interval of x seems rather large, and examination of samples around $x=0.05$ will be needed to optimize the power factor.

The electrical conductivity and Seebeck coefficient of antiferrotype Cu_2Se , the crystal structure of which consists of a three-dimensional network of edge-sharing CuSe_4 tetrahedra, were previously reported by Akkad *et al.*⁸ The monoselenide Cu_2Se was also a p -type degenerate semicon-

ductor, with the hole carrier concentration of $9.2 \times 10^{19} \text{ cm}^{-3}$ corresponding to the Cu vacancies of $\delta = 5.2 \times 10^{-3}$, which were formed unintentionally during the synthesis. The data of $\sigma \sim 200 \text{ } \Omega^{-1} \text{ cm}^{-1}$ and $S \sim 140 \text{ } \mu\text{V K}^{-1}$ at 500 K or $\sigma \sim 120 \text{ } \Omega^{-1} \text{ cm}^{-1}$ and $S \sim 185 \text{ } \mu\text{V K}^{-1}$ at 600 K give power factors of $\sim 4 \times 10^{-4} \text{ W m}^{-1} \text{ K}^{-2}$. Ohtani *et al.*¹⁴ also reported that samples of Cu_{2-x}Se having large Cu deficiencies of $x=0.20$ to 0.25 showed a metallic property with $\sigma \sim 10^4 \text{ } \Omega^{-1} \text{ cm}^{-1}$ and $S \sim 5 \text{ } \mu\text{V K}^{-1}$ at temperatures lower than 300 K , which give a power factor of $\sim 2.5 \times 10^{-5} \text{ W m}^{-1} \text{ K}^{-2}$. Thus, the power factor depends on the amount of Cu vacancies. The power factor for $\text{La}_{0.95}\text{Sr}_{0.05}\text{CuOSe}$ obtained in this study is close to that for the former Cu_2Se . A 2-D effect on the thermoelectric properties such as the carrier confinement effect was not clearly observed, and investigation using single-crystal sample will be necessary to confirm the effect on the thermoelectric properties of LaCuOSe .

Thermal conductivity for the samples with $x=0.00$ and 0.05 was estimated to be $2.1 \text{ W m}^{-1} \text{ K}^{-1}$ and $2.3 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature, respectively. A rough estimation of Z value using the σ and S data at 370 K gives $7.5 \times 10^{-7} \text{ K}^{-1}$ for $x=0.00$ and $4.4 \times 10^{-5} \text{ K}^{-1}$ for $x=0.05$. Thermal conductivity κ is expressed as a sum of the lattice part κ_{ph} and the electronic part κ_e : $\kappa = \kappa_{\text{ph}} + \kappa_e$. The κ_e can be evaluated by the Wiedemann-Franz law: $\kappa_e = L\sigma T$, where L is the Lorenz number $2.44 \times 10^{-8} \text{ V}^2 \text{ K}^{-2}$ and T is the absolute temperature.¹⁵ The κ_e value evaluated using the σ at 300 K for $x=0.05$ is approximately $8.0 \times 10^{-2} \text{ W m}^{-1} \text{ K}^{-1}$, which is approximately 3.5% of the total κ . This evaluation indicates that the phonon thermal conductivity is dominant for both the samples. Since there are a variety of compounds in the layered oxychalcogenides, formation of the solid solutions such as $\text{LaCuOS}_{1-x}\text{Se}_x$ and $\text{La}_{1-x}\text{Y}_x\text{CuOSe}$ will be effective for reduction of the phonon thermal conductivity.

IV. CONCLUSIONS

Thermoelectric properties of the layered oxyselenides $\text{La}_{1-x}\text{Sr}_x\text{CuOSe}$ were investigated as candidate thermoelectric materials. The LaCuOSe was a p -type degenerate semiconductor, whereas the Sr-doped materials with $x=0.05$ to 0.20 were p -type metals. The Sr concentration dependence of the electrical conductivity and Seebeck coefficient showed that the effective hole carriers increased with increasing doped Sr atoms up to $x=0.10$. Thermoelectric power factors were drastically enhanced by the Sr doping and maximized for $x=0.05$, the values being $1.0 - 1.4 \times 10^{-4} \text{ W m}^{-1} \text{ K}^{-2}$. Thermal conductivities for the materials with $x=0.00$ and 0.05 were $2.1 \text{ W m}^{-1} \text{ K}^{-1}$ and $2.3 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature, respectively, and the phonon thermal conductivity was dominant for both the samples. Using the κ values at room temperature and the σ and S values at 370 K , Z values for the polycrystalline $\text{La}_{1-x}\text{Sr}_x\text{CuOSe}$ were roughly estimated to be $7.5 \times 10^{-7} \text{ K}^{-1}$ for $x=0.00$ and $4.4 \times 10^{-5} \text{ K}^{-1}$ for $x=0.05$.

ACKNOWLEDGMENT

The authors are grateful to N. Murayama and W. Shin of National Institute of Advanced Industrial Science and Technology for measurements of thermal conductivity.

- ¹M. Palazzi, C. R. Acad. Sc. Paris, t. **292**, 789 (1981).
- ²W. J. Zhu, Y. Z. Huang, C. Dong, and Z. X. Zhao, Mater. Res. Bull. **29**, 143 (1994).
- ³B. A. Popovkin, A. M. Kusainova, V. A. Dolgikh, and L. G. Aksel'rud, Russ. J. Inorg. Chem. **43**, 1471 (1998).
- ⁴S. Inoue, K. Ueda, and H. Hosono, Phys. Rev. B **64**, 245211 (2001).
- ⁵Y. Takano, K. Yahagi, and K. Sekizawa, Physica B **206 & 207**, 764 (1995).
- ⁶T. Ohtani, M. Hirose, T. Sato, K. Nagaoka, and M. Iwabe, Jpn. J. Appl. Phys. **32**, Suppl. 32-3, 316 (1993).
- ⁷K. Ueda, S. Inoue, S. Hirose, H. Kawazoe, and H. Hosono, Appl. Phys. Lett. **77**, 2701 (2000); K. Ueda, S. Inoue, H. Hosono, N. Sarukura, and M. Hirano, Appl. Phys. Lett. **78**, 2333 (2001); K. Ueda and H. Hosono, J. Appl. Phys. **91**, 4768 (2002).
- ⁸F. El Akkad, B. Mansour, and T. Hendeya, Mater. Res. Bull. **16**, 535 (1981).
- ⁹R. Venkatasubramanian, E. Siivola, T. Colpitts, and B. O'Quinn, Nature (London) **413**, 597 (2001); L. D. Hicks and M. S. Dresselhaus, Phys. Rev. B **47**, 12727 (1993).
- ¹⁰K. Ishikawa, S. Kinoshita, Y. Suzuki, S. Matsuura, T. Nakanishi, M. Aizawa, and Y. Suzuki, J. Electrochem. Soc. **138**, 1166 (1991).
- ¹¹N. Cusack and P. Kendall, Proc. Phys. Soc. London **72**, 898 (1958).
- ¹²K. Ueda and H. Hosono, Thin Solid Films **411**, 115 (2002).
- ¹³R. D. Shannon, Acta Crystallogr. Sect. A, Cryst. Phys. Diffr. Theor. Gen. Crystallogr. **32**, 751 (1976).
- ¹⁴T. Ohtani, Y. Tachibana, J. Ogura, T. Miyake, Y. Okada, and Y. Yokota, J. Alloys Compd. **279**, 136 (1998).
- ¹⁵M. E. Fine and N. Hsieh, J. Am. Ceram. Soc. **57**, 502 (1974).