

Enhancement of thermoelectric properties by Se substitution in layered bismuth-chalcogenide $\text{LaOBiS}_{2-x}\text{Se}_x$

Yoshikazu Mizuguchi^{1*}, Atsushi Omachi¹, Yosuke Goto², Yoichi Kamihara², Masanori Matoba², Takafumi Hiroi¹, Joe Kajitani¹, Osuke Miura¹

1. Department of Electrical and Electronic Engineering, Tokyo Metropolitan University,
1-1, Minami-osawa, Hachioji 192-0397, Japan

2. Department of Applied Physics and Physico-Informatics, Keio University, 3-14-1
Hiyoshi, Yokohama 223-8522, Japan

Corresponding author: Yoshikazu Mizuguchi (mizugu@tmu.ac.jp)

Abstract

We have investigated the thermoelectric properties of the novel layered bismuth chalcogenides $\text{LaOBiS}_{2-x}\text{Se}_x$. The partial substitution of S by Se produced the enhancement of electrical conductivity (metallic characteristics) in $\text{LaOBiS}_{2-x}\text{Se}_x$. The power factor largely increased with increasing Se concentration. The highest power factor was $4.5 \mu\text{W}/\text{cmK}^2$ at around 470°C for $\text{LaOBiS}_{1.2}\text{Se}_{0.8}$. The obtained dimensionless figure-of-merit (ZT) was 0.17 at around 470°C in $\text{LaOBiS}_{1.2}\text{Se}_{0.8}$.

Discovery of novel thermoelectric materials with a high performance is one of the most important issues for the development of thermoelectric application [1]. In recent years, researchers have focused on layered materials as candidates of a novel thermoelectric material because their low-dimensional crystal structure and electronic states can produce a high thermoelectric property as realized in Bi_2Te_3 , cobalt oxides and CsBi_4Te_6 [2-4].

Since 2012, layered compounds with the BiS_2 layers have got much attention in the field of condensed matter physics due to the discovery of superconductivity with a transition temperature as high as 11 K in $\text{Bi}_4\text{O}_4\text{S}_3$ [5], $\text{REO}_{1-x}\text{F}_x\text{BiS}_2$ ($\text{RE} = \text{La, Ce, Pr, Nd and Yb}$) [6-12] and $\text{AE}_{1-x}\text{RE}_x\text{FBiS}_2$ ($\text{AE} = \text{Sr and Eu}$) [13-16]. Their crystal structure is basically composed of alternate stacks of the conduction layer (BiS_2 layer) and the blocking layer such as REO layer. In the BiS_2 -based materials, the Bi- $6p$ orbitals within the BiS_2 layer are essential for electronic conduction. It has been revealed that the electronic states are easily tunable by element substitutions at the blocking layers. Having considered the low-dimensional crystal structure and electronic states, we have regarded the layered bismuth chalcogenides as potential thermoelectric materials.

In the previous study, we investigated physical properties of the BiS_2 -based layered compounds $\text{LaO}_{1-x}\text{F}_x\text{BiS}_2$ at high temperatures [17]. We observed an anomalous metallic behavior in LaOBiS_2 : a metal-semiconductor transition was revealed at around 270 K. The highest power factor of $1.9 \mu\text{W/cmK}^2$ at $\sim 480^\circ\text{C}$ was observed for LaOBiS_2 . In addition, we investigated the effect of F substitution (electron doping) on the power factor in $\text{LaO}_{1-x}\text{F}_x\text{BiS}_2$. Although the electrical conductivity increases by the partial substitution of O by F, the Seebeck coefficient largely decreases. Hence, the F substitution resulted in a decrease of power factor. This result suggests that the element substitution at the blocking layer negatively works in enhancing thermoelectric properties. Therefore, we have investigated the effects of element substitution at the BiS_2 conduction layer on thermoelectric properties of LaOBiS_2 . Here, we report a large enhancement of the power factor and the dimensionless figure-of-merit (ZT) by a partial substitution of S by Se in $\text{LaOBiS}_{2-x}\text{Se}_x$. On the basis of the systematic changes in lattice constants, we have considered that the S and Se ions are mixed as shown in Fig. 1(a). The partial Se substitution achieves both metallic conductivity and a large Seebeck coefficient in $\text{LaOBiS}_{2-x}\text{Se}_x$.

Polycrystalline samples of $\text{LaOBiS}_{2-x}\text{Se}_x$ were prepared by the solid-state reaction method using powders of La_2S_3 (99.9 %), La_2O_3 (99.9 %), Bi_2S_3 , Bi_2Se_3 and grains of Bi (99.999 %). The Bi_2S_3 and Bi_2Se_3 powders were synthesized by reacting Bi, S (99.99 %)

or Se (99.99 %) grains in an evacuated quartz tube. Other chemicals were purchased from Kojundo-Kagaku Laboratory. The mixture of starting materials with nominal compositions of $\text{LaOBiS}_{2-x}\text{Se}_x$ ($x = 0, 0.2, 0.6, 0.8$ and 1.0) was mixed-well, pelletized and sealed into an evacuated quartz tube. The samples were heated at $700\text{ }^\circ\text{C}$ for 15 h . The obtained products were ground, pelletized, sealed into an evacuated quartz tube and heated under the same heating conditions for homogenization. The prepared samples were characterized by powder x-ray diffraction (XRD) with a $\text{CuK}\alpha$ radiation using the $\theta\text{-}2\theta$ method.

The XRD patterns of the typical $\text{LaOBiS}_{2-x}\text{Se}_x$ samples ($x = 0$ and 1.0) are shown in Fig. 1(b). Almost single-phase samples were obtained for $x = 0 - 1.0$, except for a small amount of La-oxide impurities as indicated by asterisk in the XRD pattern. The numbers in the XRD pattern is Miller indices with the space group of $P4/nmm$. Although we attempted to prepare the samples with $x = 1.5$ and 2.0 , single-phase samples were not obtained probably due to the existence of a solubility limit of Se for the S site in $\text{LaOBiS}_{2-x}\text{Se}_x$. The lattice constants of a and c were calculated using the peak positions of the (200) and (003) peaks, and plotted in Fig. 1(c) and 1(d), respectively. We have corrected the peak positions using the corrected data obtained from the peak position of Si [14]. Both the lattice constants of a and c increase with increasing Se concentration. The increase of lattice volume can be understood by the difference in the ionic radius of S^{2-} and Se^{2-} .

The electrical resistivity and the Seebeck coefficient were measured by the four-terminal method using ULVAC-RIKO ZEM-3 up to $480\text{ }^\circ\text{C}$ in an atmosphere of low-pressure He gas. The measurements of the thermal conductivity (κ) was conducted at temperatures up to $400\text{ }^\circ\text{C}$ using a lamp heating unit (Ulvac, MILA-5000). The κ was obtained from the slopes of the plots of heat flux density vs. ΔT using a strain gauge as a heater and was measured under pressures less than 10^{-3} Pa . The heat loss by radiation through the samples [18] was subtracted under the assumption that emissivity is independent of temperature and wavelength during the measurements of κ . The emissivity of 0.8 was employed on the basis of reflectivity measurements, which were performed at room temperature using a spectrometer equipped with an integrating sphere (Hitachi High-tech, U-4100). The relative density of the sintered pellet used in these measurements is ~85 % (84 % for $x = 0$ and 91 % for $x = 1.0$).

The power factor was calculated using an equation $P = S^2/\rho$, where S and ρ are Seebeck coefficient and electrical resistivity, respectively. The dimensionless figure-of-merit was calculated using an equation of $ZT = P T / \kappa$, where κ and T are thermal conductivity

and absolute temperature, respectively.

Figure 2(a) shows the temperature dependences of electrical resistivity for $\text{LaOBiS}_{2-x}\text{Se}_x$. An anomaly is observed at around 400 °C for $x = 0.2$, which is similar to those observed at around 200 °C in $x = 0$ (LaOBiS_2) and F-doped LaOBiS_2 [17]. The anomaly may be related to a charge-density-wave transition, which was recently observed in EuFBiS_2 [16]. In the temperature dependences for $x = 0.6, 0.8$ and 1.0 , metallic behavior is observed without any anomalies below 480 °C. With increasing Se concentration, the values of electrical resistivity systematically decrease, indicating that the Se substitution enhances metallic characteristics. The value of electrical resistivity at around 470 °C for LaOBiSSe ($x = 1.0$) is $\sim 4.7 \text{ m}\Omega\text{cm}$, which is clearly lower than that for LaOBiS_2 ($x = 0$) ($\sim 21 \text{ m}\Omega\text{cm}$) [17]. To clarify the mechanism of the enhancement of electrical conductivity by Se substitution, investigations with single crystals and band calculations are needed.

Figure 2(b) shows the temperature dependences of Seebeck coefficient for $\text{LaOBiS}_{2-x}\text{Se}_x$. All the samples show negative Seebeck coefficient, indicating that the contributing carrier is basically electron. The absolute value of the Seebeck coefficient tends to increase with increasing temperature for all the samples. Although the absolute values of Seebeck coefficient decrease with increasing Se concentration, the values at around 470 °C for $x = 0.8$ and 1.0 are still around $-150 \mu\text{V/K}$, which is a relatively high value as a metallic compound.

The obtained power factors are plotted in Fig. 2(c) as a function of temperature. The values of power factor are largely enhanced by Se substitution. For $x = 0.2$ and 0.6 , the temperature dependence of power factor shows a maximum at around 200 - 300 °C. For $x = 0.8$ and 1.0 , the values of power factor monotonously increase with increasing temperature within a range of $T < 480$ °C. The highest power factor is $4.5 \mu\text{W/cmK}^2$ at around 470 °C for $x = 1.0$ (LaOBiSSe). This value is 237 % of the highest value obtained in LaOBiS_2 .

Finally, we discuss the thermoelectric performance of the $\text{LaOBiS}_{2-x}\text{Se}_x$ system. In order to calculate the dimensionless figure-of-merit (ZT), we have measured thermal conductivity for the end members ($x = 0$ and 1.0). Figure 3(a) shows the temperature dependences of thermal conductivity for $x = 0$ and 1.0 . It is found that the thermal conductivity for $\text{LaOBiS}_{2-x}\text{Se}_x$ is almost independent of temperature. Furthermore, the obtained values of thermal conductivity are almost the same for LaOBiS_2 and LaOBiSSe , indicating that the partial substitution of S by Se does not affect the thermal conductivity in this system. In general, electronic thermal conductivity increases with enhancing metallic characteristics. On another front, the phonon thermal conductivity

could decrease by substituting the chalcogen site in $\text{LaOBiS}_{2-x}\text{Se}_x$ due to introduction of the randomness. Hence, it is considered that the total thermal conductivity does not change with increasing Se concentration because of the compensation of the changes in the electron thermal conductivity and the phonon thermal conductivity. Therefore, we use a typical (average) value of $\kappa = 2 \text{ W/m K}$, which is the value estimated at room temperature for LaOBiS_2 and LaOBiSSe , to estimate ZT . This κ value is consistent with that reported in the previous study on low-temperature thermal properties of LaOBiS_2 [19]. The temperature dependences of dimensionless figure-of-merit (ZT) for $\text{LaOBiS}_{2-x}\text{Se}_x$ are plotted in Fig. 3(b). For all the samples, the value of ZT tends to increase with increasing temperature, and it reaches a maximum value at around 470 °C, which is the measurement limit of the present work. This fact indicates that the $\text{LaOBiS}_{2-x}\text{Se}_x$ system is a potential thermoelectric material for the use at high temperatures. The highest value of ZT is 0.17 for $x = 0.8$ ($\text{LaOBiS}_{1.2}\text{Se}_{0.8}$) at 470 °C. To further increase the thermoelectric performance in this family, precise tuning of carrier concentration and/or local crystal structure are needed. In this family, partial substitutions at the blocking layer can tune both the carrier concentration within the conduction layers and the local structure that largely affects the physical properties [6, 17, 20]. Therefore, a strategy to enhance the thermoelectric performance of this system will be tuning of the structure of the blocking layer.

In conclusion, we have synthesized polycrystalline samples of novel layered bismuth chalcogenides $\text{LaOBiS}_{2-x}\text{Se}_x$ and systematically investigated thermoelectric properties. It was found that a partial substitution of S by Se enhanced metallic conductivity. The power factor largely increased with increasing Se concentration. The highest power factor was $4.5 \mu\text{W/cmK}^2$ at around 470 °C for $\text{LaOBiS}_{1.2}\text{Se}_{0.8}$. We found that the thermal conductivity for $\text{LaOBiS}_{2-x}\text{Se}_x$ is independent of both temperature and Se concentration. Using an average value of thermal conductivity, $\kappa = 2 \text{ W/m K}$, we calculated the dimensionless figure-of-merit (ZT) as a function of temperature. The highest ZT was 0.17 at around 470 °C in $\text{LaOBiS}_{1.2}\text{Se}_{0.8}$. Optimization of the carrier concentration and/or the local structure will further enhance the thermoelectric performance of the layered bismuth chalcogenides.

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Figure captions

Fig. 1. (a) Schematic image of the crystal structure of $\text{LaOBiS}_{2-x}\text{Se}_x$. (b) Powder XRD patterns for the end members LaOBiS_2 and LaOBiSSe ($x = 0$ and 1.0). (c) Se concentration dependence of lattice constant of a for $\text{LaOBiS}_{2-x}\text{Se}_x$. (d) Se concentration dependence of lattice constant of c for $\text{LaOBiS}_{2-x}\text{Se}_x$.

Fig. 2. (a) Temperature dependences of electrical resistivity for $\text{LaOBiS}_{2-x}\text{Se}_x$. (b) Temperature dependences of Seebeck coefficient for $\text{LaOBiS}_{2-x}\text{Se}_x$. (c) Temperature dependences of power factor for $\text{LaOBiS}_{2-x}\text{Se}_x$.

Fig. 3. (a) Temperature dependences of thermal conductivity for LaOBiS_2 and LaOBiSSe ($x = 0$ and 1.0). (b) Temperature dependences of ZT for $\text{LaOBiS}_{2-x}\text{Se}_x$.

Fig. 1(a)

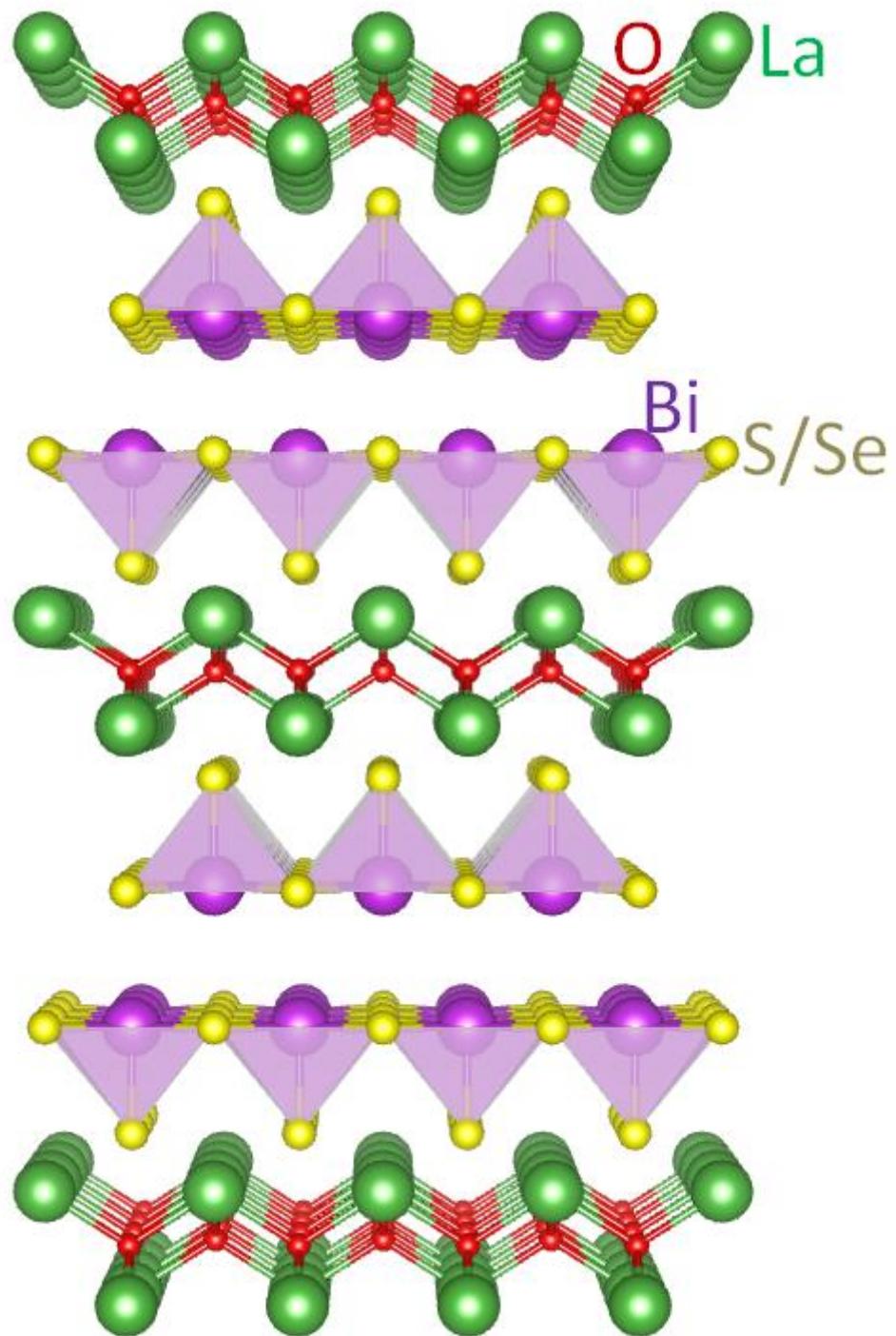


Fig. 1(b)

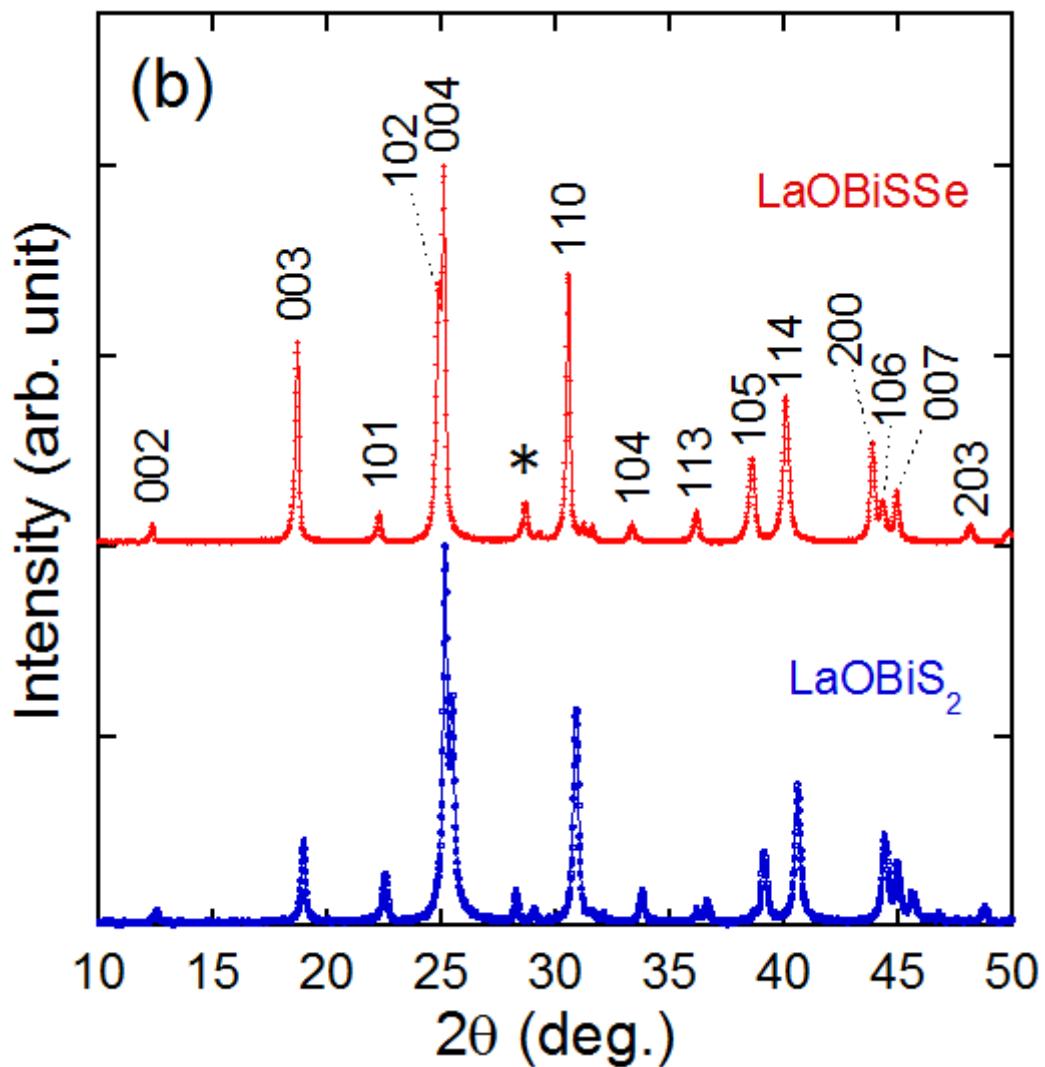


Fig. 1(c,d)

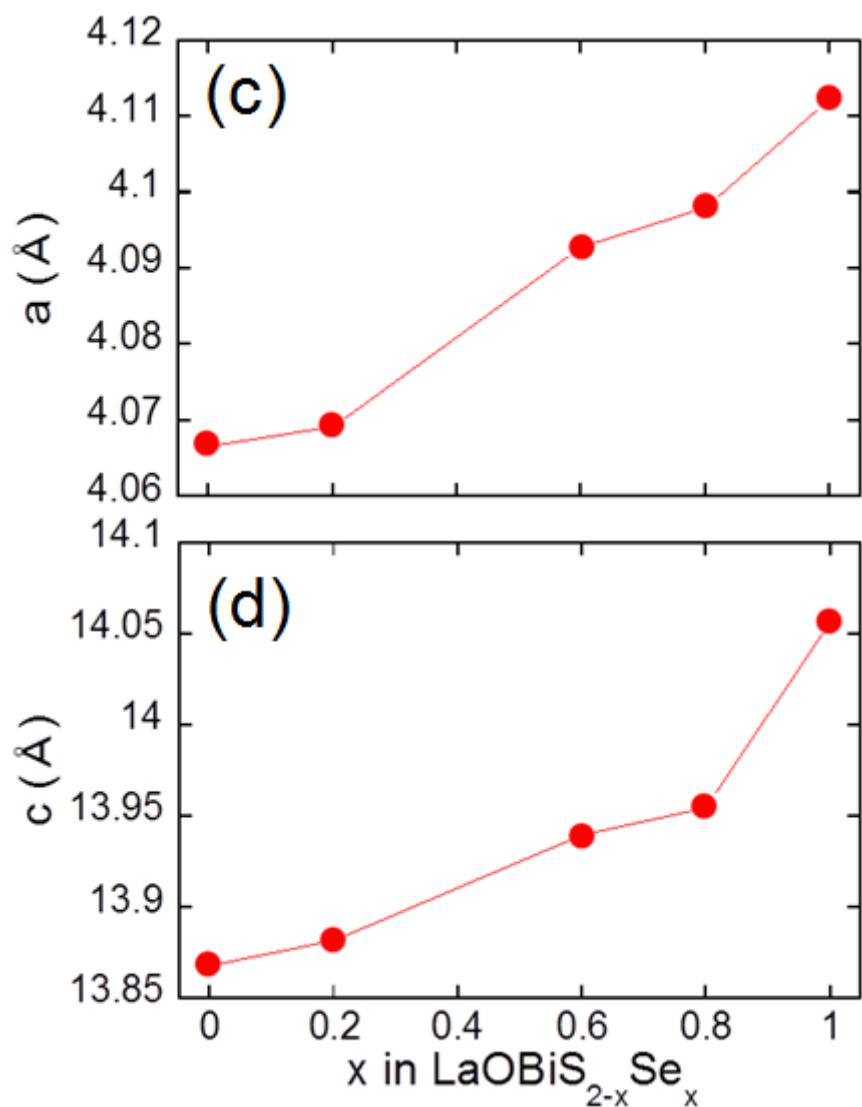


Fig. 4

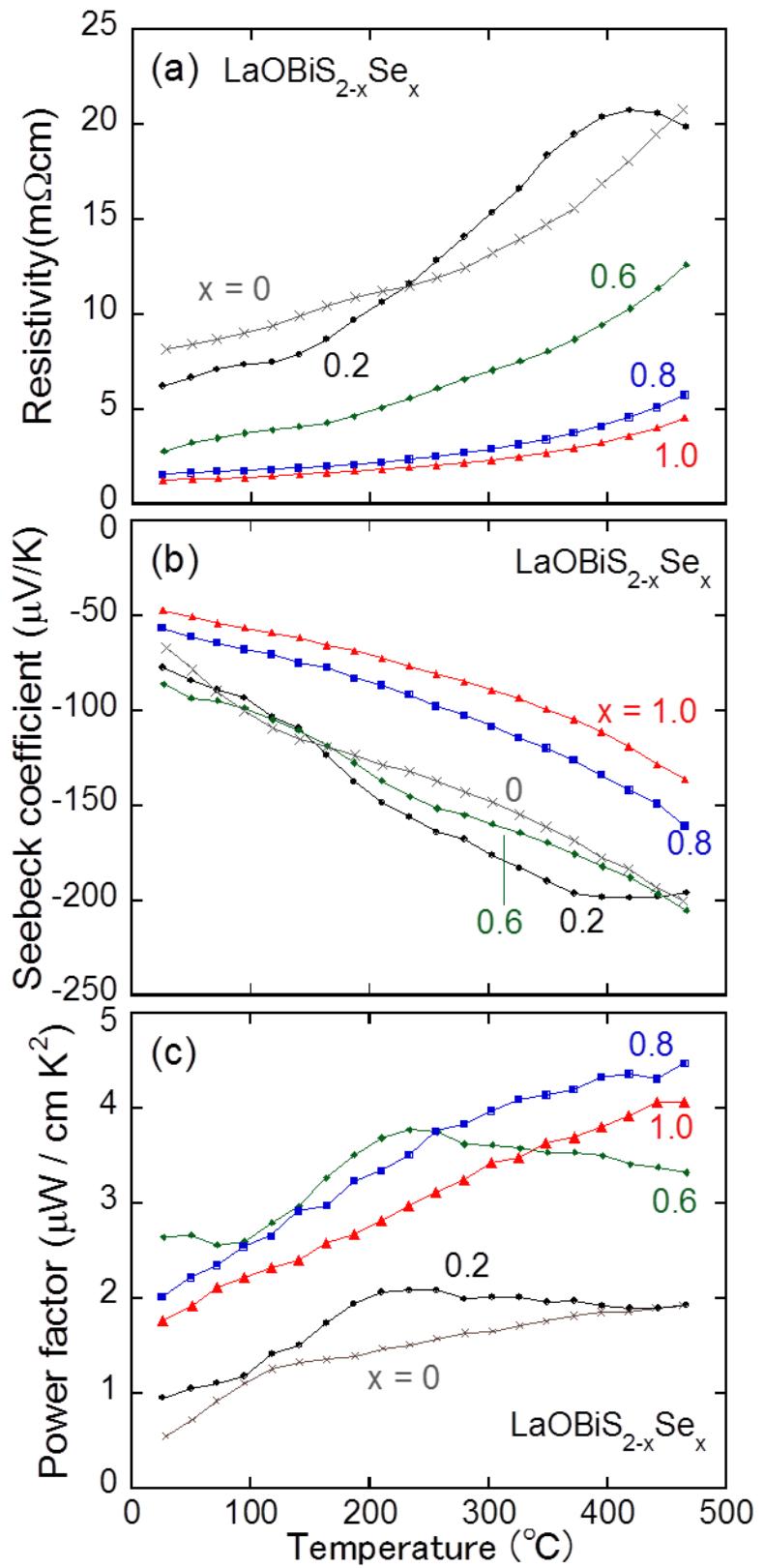


Fig. 5

