

High-temperature thermoelectric properties of novel layered bismuth-sulfide $\text{LaO}_{1-x}\text{F}_x\text{BiS}_2$

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Abstract

We have investigated the high-temperature thermoelectric properties of the layered compound $\text{LaO}_{1-x}\text{F}_x\text{BiS}_2$. The electrical resistivity of LaOBiS_2 showed an anomalous behavior; a metal-semiconductor transition was observed around 270 K. It was found that the value of the electrical resistivity decreased with F substitution. The Seebeck coefficient decreased with increasing F concentration. The highest power factor of 1.9 $\mu\text{W}/\text{cmK}^2$ at 480 °C was obtained for LaOBiS_2 .

1. Introduction

Discovery of novel thermoelectric material is one of the most important issues for development of thermoelectric application [1]. Particularly, layered materials have been actively studied because their low-dimensional electronic states could result in high thermoelectric properties as realized in Bi₂Te₃, cobalt oxides and CsBi₄Te₆ [2-4]. Recently, layered compounds with BiS₂ layers have got much attention because two-dimensional superconductivity with transition temperature as high as 10.6 K was observed [5-13]. Among the BiS₂-based layered compounds, LaOBiS₂ is the typical system, and it has mostly studied in this one year [6,11]. The schematic image of the crystal structure of LaOBiS₂ is shown in Fig. 1. It is composed of an alternate stacking of the conduction layer (BiS₂ layer) and the blocking layer (LaO layer). Recently, we found that the electrical resistivity shows an anomalous behavior. Figure 2 shows the temperature dependence of resistivity for the polycrystalline sample of LaOBiS₂. The resistivity decreases on cooling above 270 K while the resistivity shows a semiconducting behavior below 270 K. Because of the layered structure and the observed anomalous characteristics on the electrical conductivity, we have expected that pristine or carrier-doped LaOBiS₂ could be a potential candidate for novel thermoelectric materials. Here, we show the thermoelectric properties at high temperatures for LaO_{1-x}F_xBiS₂.

2. Methods

Polycrystalline samples of LaO_{1-x}F_xBiS₂ were prepared by the solid-state reaction method using powders of La₂S₃ (99.9 %), Bi₂O₃ (99.9 %), BiF₃ (99.9 %), Bi₂S₃ and grains of Bi (99.99 %). The Bi₂S₃ powder was synthesized by reacting Bi (99.99 %) and S (99.99 %) grains at 800 °C in an evacuated quartz tube. Other chemicals were purchased from Kojundo-Kagaku Laboratory. The mixture of starting materials with nominal compositions of LaO_{1-x}F_xBiS₂ ($x = 0, 0.05, 0.25, 0.5$) was well mixed, pelletized and sealed into an evacuated quartz tube. The LaO_{1-x}F_xBiS₂ pellets were heated at 800 °C for 15h. The obtained samples were ground, pelletized, sealed into an evacuated quarts tube and heated under the same heating conditions to homogenize the samples.

The prepared samples were characterized by powder x-ray diffraction with CuK α radiation using RIGAKU Smart-Lab. The electrical resistivity and the Seebeck coefficient were measured by the four-terminal method using ULVAC-RIKO ZEM-3 up to 480 °C in an atmosphere of low-pressure He gas.

3. Results and discussion

Figure 3 shows the powder x-ray diffraction patterns for $\text{LaO}_{1-x}\text{F}_x\text{BiS}_2$. Almost all of the peaks were indexed using the tetragonal space group of $P4/nmm$. For $x=0$ and 0.05 , small peaks of the impurity $\text{La}_2\text{O}_2\text{S}$ were detected as indicated with the “+” symbols in Fig. 3. It should be noted that the $\text{La}_2\text{O}_2\text{S}$ impurity is insulator. Hence, the impurity phase does not affect the thermoelectric properties. The lattice constants a and c were calculated using the peak positions of the (200) and (004) peaks. The calculated lattice constants are displayed in Fig. 4. With increasing F concentration, the length of the c axis continuously decreases while the length of the a axis does not show a remarkable change. The changes in the lattice constants upon F substitutions are consistent with the previous experiments [14,15].

Figure 5 shows the temperature dependence of the electrical resistivity for $\text{LaO}_{1-x}\text{F}_x\text{BiS}_2$. With increasing F concentration, the value of resistivity decreases at whole temperatures. This fact is consistent with the scenario that the electron carriers could be generated in the BiS_2 layers upon F substitution. For $x=0$, the resistivity increases with increasing temperature, which is a metallic behavior. For $x=0.05 - 0.5$, the temperature dependence of the resistivity does not show small remarkable changes with increasing temperature. For all the samples, humps are observed as indicated with the triangle symbols in Fig. 5. The hump shifts to a higher temperature with increasing F concentration. The hump may indicate the evolution of ordered states something like charge-density-wave state which have been theoretically predicted to be possible to occur in the BiS_2 -based family.

Figure 6 shows the temperature dependence of the Seebeck coefficient for $\text{LaO}_{1-x}\text{F}_x\text{BiS}_2$. For all the samples, the Seebeck coefficient increases with increasing temperature. The value of the Seebeck coefficient decreases with increasing F concentration. The highest Seebeck coefficient of $200 \mu\text{V/K}$ was observed at 480°C for $x=0$.

The power factor was calculated using the equation of $P = S^2/\rho$ (P : power factor, S : Seebeck coefficient, ρ : electrical resistivity). Figure 7 shows the temperature dependence of the power factor for $\text{LaO}_{1-x}\text{F}_x\text{BiS}_2$. For all samples, the power factor increases with increasing temperature. With increasing F concentration, the power factor decreases. The highest power factor of $1.9 \mu\text{W/cmK}^2$ at 480°C is obtained for $x=0$.

Although the obtained power factor of LaOBiS₂ is much lower than that of thermoelectric materials used in a practical application and the partial F substitution is not effective for enhancing power factor, we believe that further improvement of the power factor in this material is possible. Since this material possesses a layered structure, we will be able to tune the physical properties by manipulating the blocking layer. A partial or full substitution of the La site by other lanthanide elements, such as La_{1-x}*Ln*_xOBiS₂ (*Ln* = lanthanide), will generate a chemical pressure effect. Further, a partial substitution of La by alkaline earth elements, such as La_{1-x}*A*_xOBiS₂ (*A* = alkaline earth metal) will provide hole carriers in the BiS₂ layers. Another strategy is a replacement of the blocking layer structure. If a blocking layer thicker along the *c* axis could be inserted between conduction layers, two-dimensionality should be enhanced and the thermoelectric properties may be enhanced.

4. Conclusion

We have synthesized the polycrystalline samples of new layered bismuth-sulfide LaO_{1-x}F_xBiS₂. To investigate the thermoelectric properties, the electrical resistivity and Seebeck coefficient at high temperature up to 480 °C were measured. LaOBiS₂ showed a metallic behavior of electrical resistivity above 270 K while it showed a semiconducting behavior below 270 K. It was found that the value of the electrical resistivity decreased with F substitution. The Seebeck coefficient decreased with increasing F concentration. The highest power factor of 1.9 μW/cmK² at 480 °C was obtained for LaOBiS₂. Although the obtained power factor was lower than those of the thermoelectric materials on practical use, we will be able to improve the thermoelectric properties by manipulating the blocking layer in the BiS₂-based layered family.

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Figure captions

Fig. 1. Schematic image of the crystal structure of LaOBiS_2 .

Fig. 2. Temperature dependence of the resistivity for LaOBiS_2 .

Fig. 3. Powder x-ray diffraction patterns for $\text{LaO}_{1-x}\text{F}_x\text{BiS}_2$. The numbers shown with $x=0.5$ are Miller indices. The peaks of impurity $\text{La}_2\text{O}_2\text{S}$ are indicated with “+”.

Fig. 4. (a) F concentration dependence of lattice constant a for $\text{LaO}_{1-x}\text{F}_x\text{BiS}_2$. (b) F concentration dependence of lattice constant c for $\text{LaO}_{1-x}\text{F}_x\text{BiS}_2$.

Fig. 5. Temperature dependence of electrical resistivity for $\text{LaO}_{1-x}\text{F}_x\text{BiS}_2$. The triangle symbol indicates the temperature of the apical of the anomaly.

Fig. 6. Temperature dependence of the Seebeck coefficient for $\text{LaO}_{1-x}\text{F}_x\text{BiS}_2$.

Fig. 7. Temperature dependence of the Power factor for $\text{LaO}_{1-x}\text{F}_x\text{BiS}_2$.

Fig. 1.

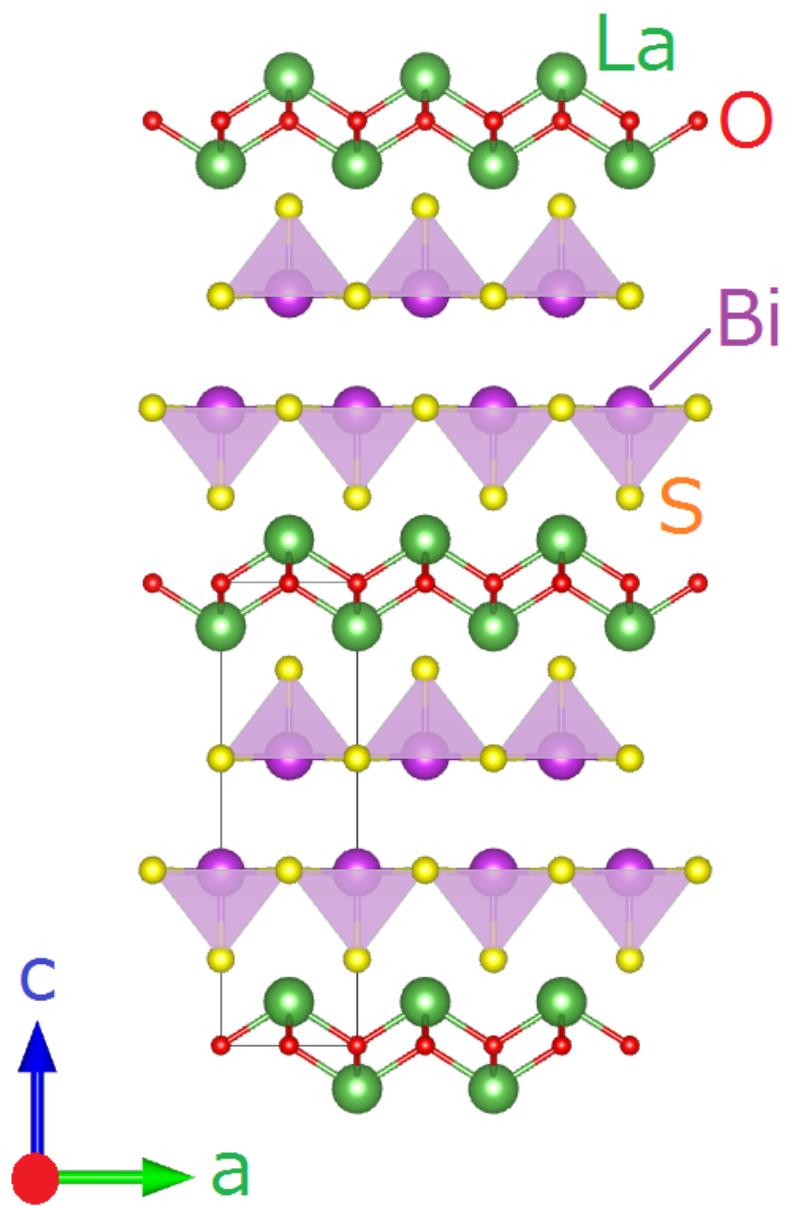


Fig. 2.

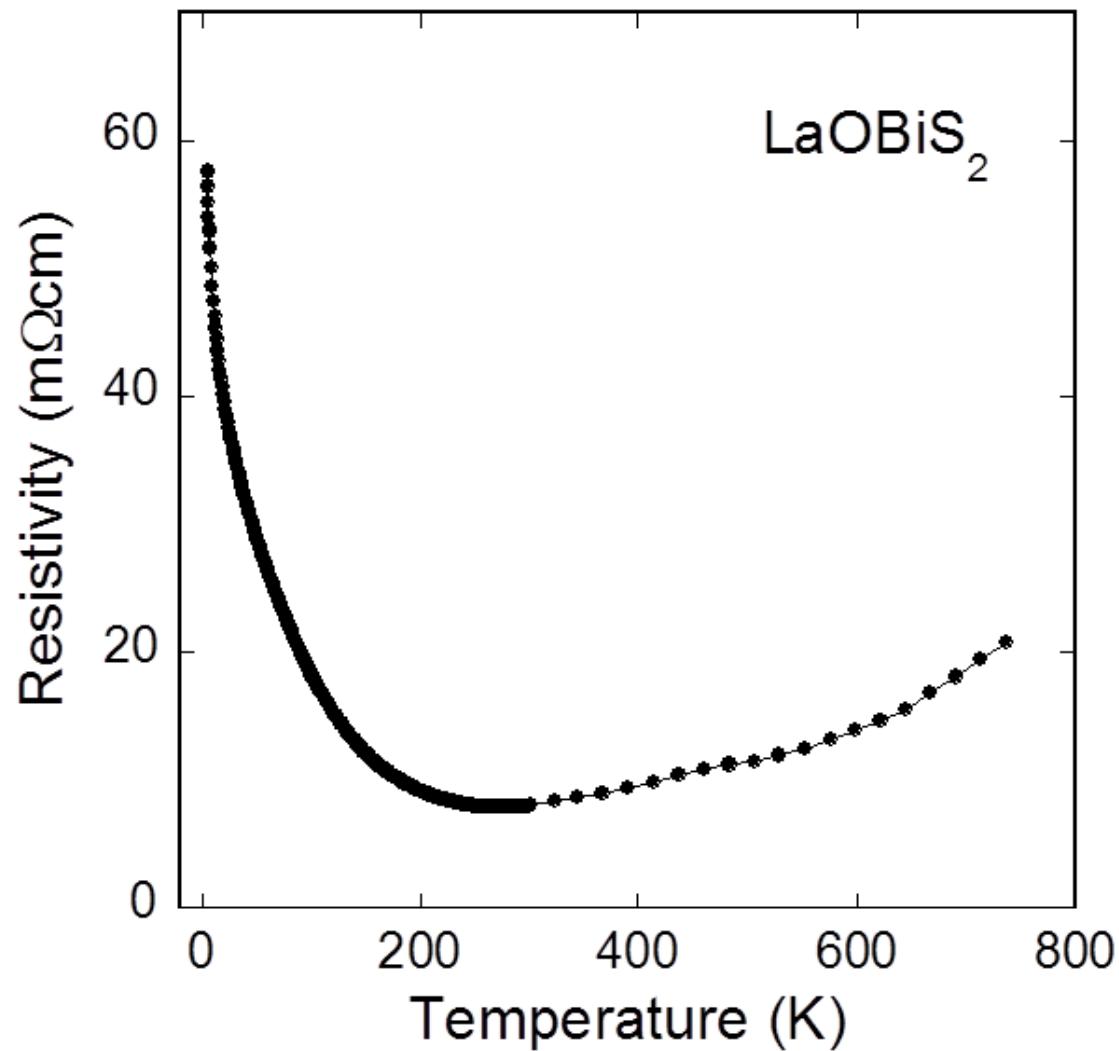


Fig. 3.

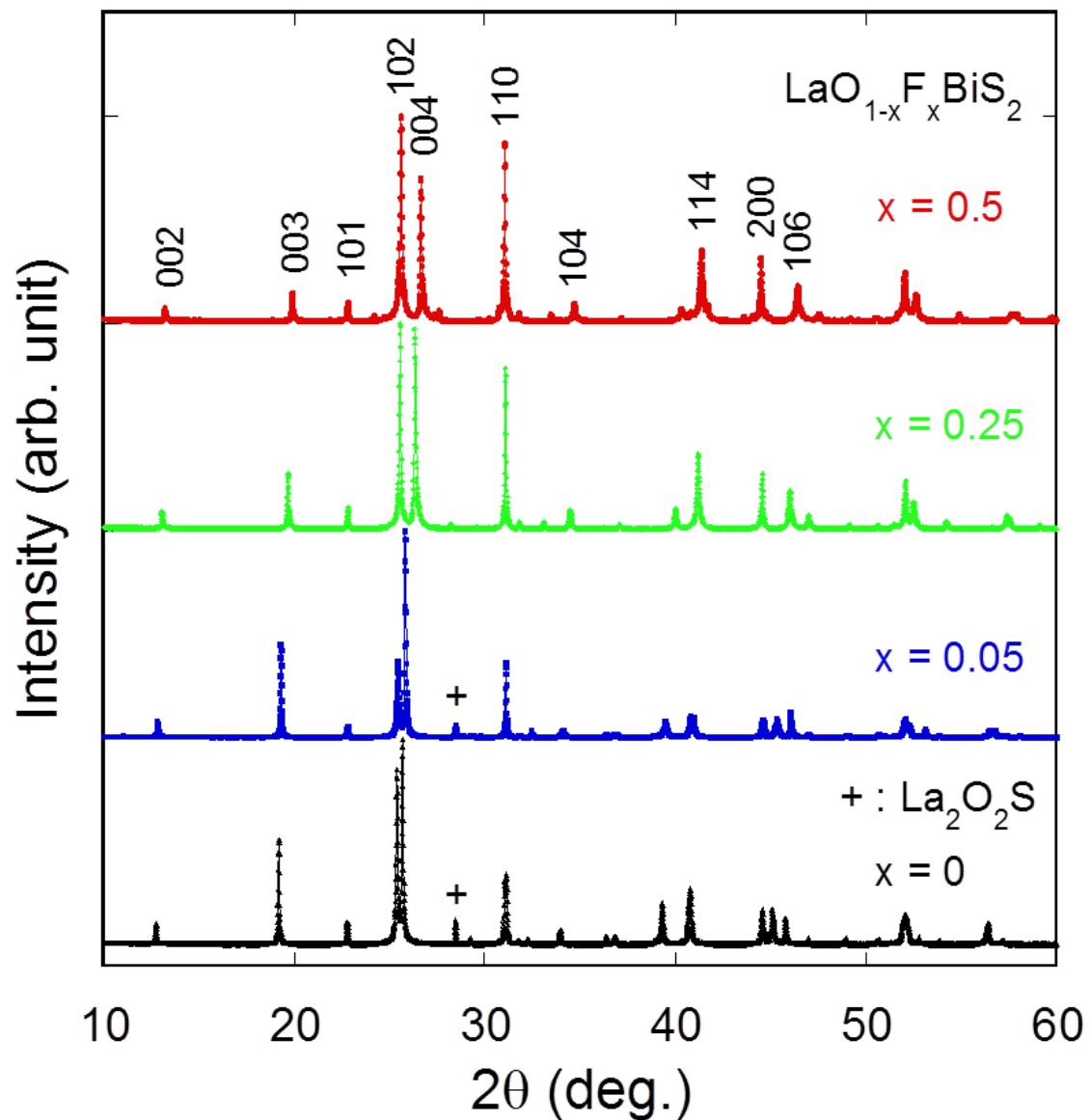


Fig. 4.

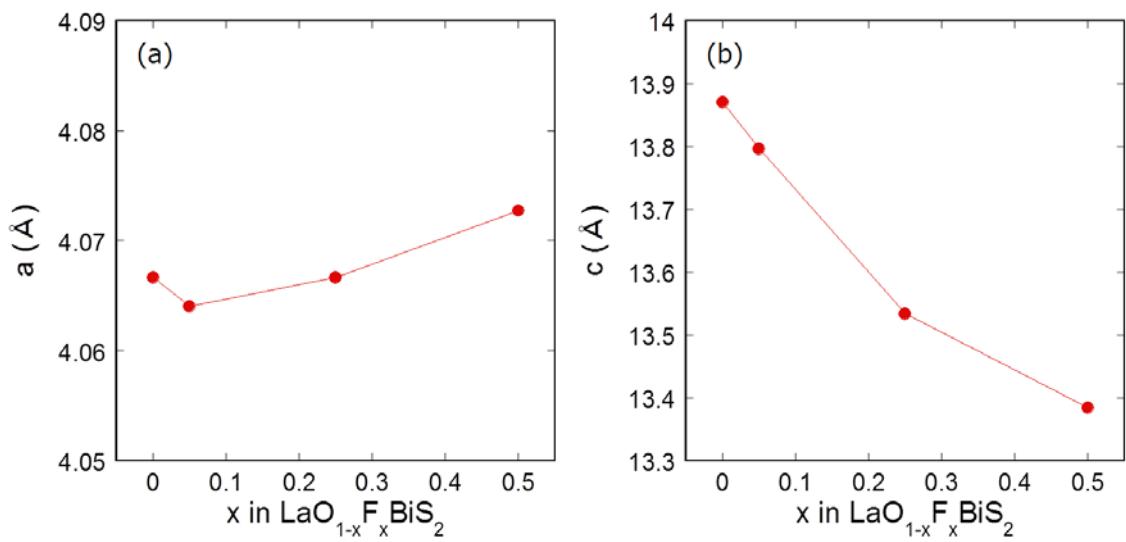


Fig. 5.

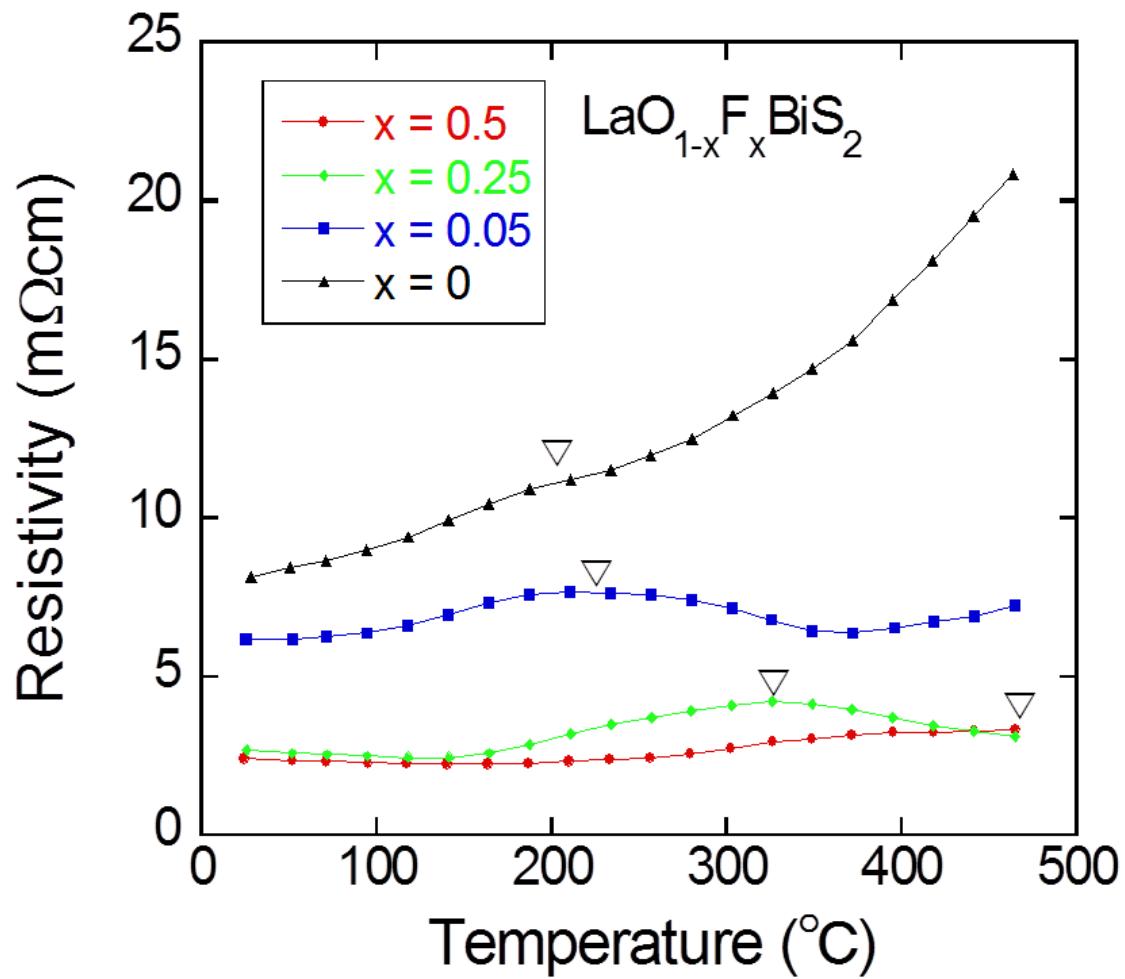


Fig. 6.

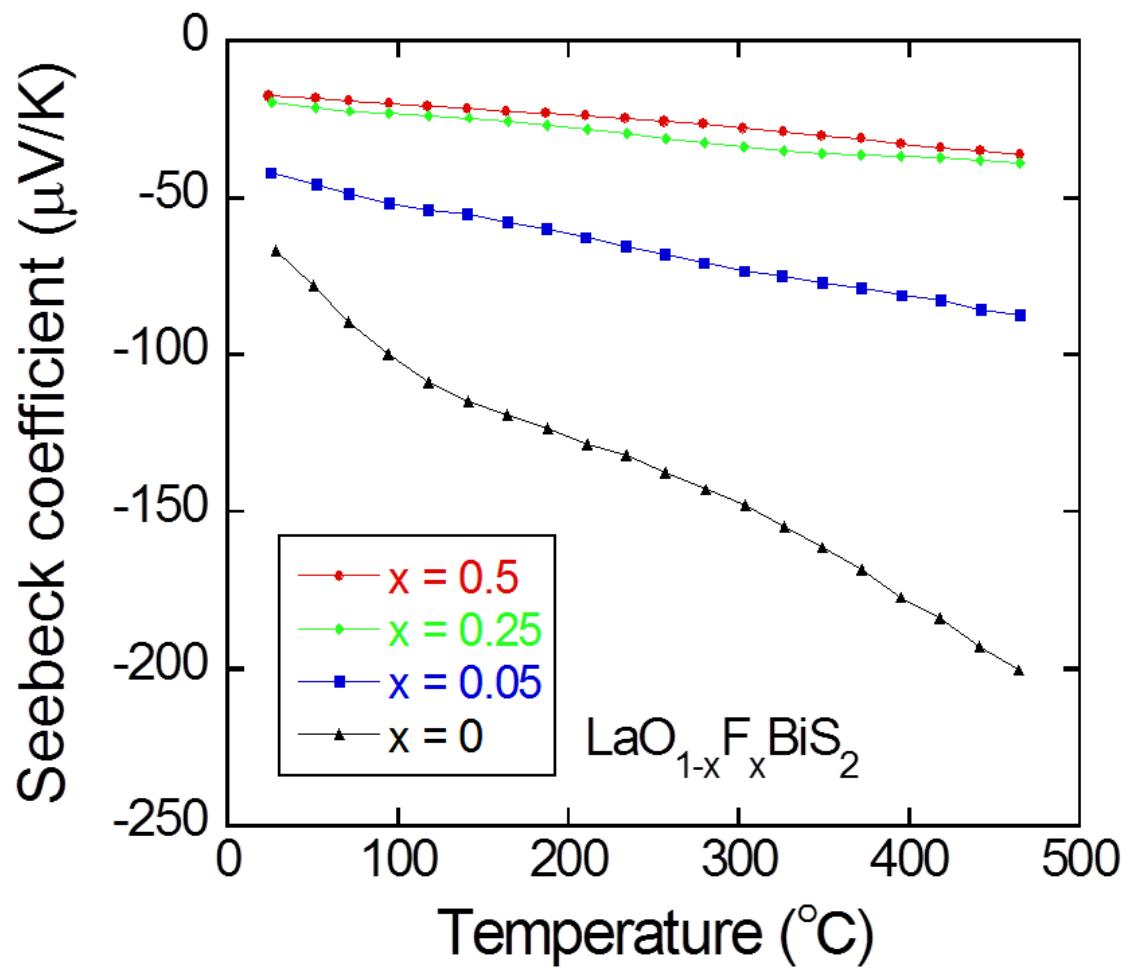


Fig. 7.

