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Michihiro Ohta,[a] Shinji Hirai, and Hisanaga Kato
Department of Materials Science and Enginnering, Muroran Institute of Technology, Muroran, Hokkaido 050-8585, Japan

Toshiyuki Nishimura and Yoichiro Uemura
Advanced Materials Laboratory, National Institute for Materials Science, Tsukuba, Ibaraki 305-0044, Japan

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The electrical resistivity, thermopower, and thermal conductivity have been measured for the lanthanum sesquisulfide (La_2S_3) of which the crystal phase is controlled by the Ti additive. In all the samples, the thermopower is negative between 300 and 1000 K. The sample with 8 wt % Ti, which consists almost of the cubic γ phase, behaves as a degenerate semiconductor. The thermoelectric figure of merit ZT increases with increasing temperature, reaching a value of 0.21 at 1000 K. In contrast, the sample with 2 wt % Ti consists almost of the tetragonal β phase. The transport mechanism can be well explained by the model of the Anderson localization. The ZT value increases abruptly with increasing temperature. At 1000 K, this ZT value is comparable with that of the sample with 8 wt % Ti. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1999845]

The γ phase of lanthanum sesquisulfide is important high-temperature thermoelectric material because of its high melting point, low phonon thermal conductivity, and degenerate semiconducting behavior.[1–3] The γ phase crystallizes in the cubic Th_3P_4 structure over the compositional range $La_2S_{2.67}$-La_2S_3.[4] The highest figure of merit ZT ($=S^2T/\rho\kappa$, where S is the thermopower, T the absolute temperature, ρ the electrical resistivity, κ the thermal conductivity) has been found in the γ phase with high sulfur content. Wood *et al.*[2] and Gadzhiev *et al.*[3] have reported the ZT values of 0.5-0.6 for $La_2S_{2.96}$ at 1000 K.

In contrast, few studies have been carried out on the electrical properties of tetragonal β phase. Since the O atom occupies a special position at the center of a regular tetrahedron of La atoms, the β phase is actually $La_{10}S_{15-y}O_y$ with $0 \leqslant y \leqslant 1$.[5,6] The substitutional oxygen has influence on the phase transformation of $La_{10}S_{15-y}O_y$. While the β phase with $y=0$ (La_2S_3) transforms to the γ phase at 1573 K, the β phase with $y=1$ ($La_{10}S_{14}O$) is stabilized in this phase over a wide range of temperatures.[5,7] Beaudry *et al.*[8] reported that the β phase is formed in the grain boundaries after extended heating of the γ phase at 1173 K and above. The presence of the β phase degrades the thermoelectric performance of the γ phase.[9]

The first attempt to improve the thermoelectric properties of the γ phase by the addition of Ti has been made by Raag and Borodovsky.[10] The preliminary result implies this potential usefulness for high-temperature thermoelectric conversion. In a previous article, we have reported the control of the β to γ phase transformation with the Ti additive.[11] The substitutional oxygen has no effect on this phase transformation. Moreover, we found that the ZT value of the γ phase with Ti is relatively large at room temperature.[12]

In the present letter, we report measurement of the electrical resistivity, thermopower, and thermal conductivity for the samples where the crystal phase is controlled by the Ti additive. We show that the improvement with respect to the thermoelectric properties of the γ phase is realized by the phase transformation due to the Ti additive. Moreover, this letter reports for the first time the thermoelectric properties of the β phase.

The $La_{10}S_{14}O$ and Ti powders were obtained from Kojundo Chemical Laboratory Co. The lanthanum, sulfur, and oxygen contents in the $La_{10}S_{14}O$ powder were verified by chemical analysis. The Ti powder was sieved to yield 45 μm. After a thorough mixing, the powders were consolidated by a pulse electric current sintering (PECS; SPS-511S, Sumitomo Coal Mining Co.). The chamber of PECS apparatus was pumped down to 7×10^{-3} Pa. The sintering was performed at 1573 K for 3.6 ks under the applied pressure of 50 MPa. The heating and cooling rates were 0.42 and 0.83 K s^{-1}, respectively. The density of the samples was calculated from the measured weight and dimensions. The crystal phase was studied by x-ray diffractometry (Rint-Ultima+, Rigaku Co.) using Cu K_α radiation.

The electrical resistivity and thermal conductivity measurements were made using a four-probe dc technique and a laser-flash method, respectively. These measurements were carried out in a vacuum chamber evacuated to less than 1.0 Pa. In order to investigate the stability during heat treatment, the electrical resistivity was measured during heating and successive cooling through 300 and 1000 K. The heating and cooling rates of 0.083 K s^{-1} were used. The Seebeck voltage was measured in a helium atmosphere. The temperature gradient across the length of the sample was varied from 0 to 10 K. The thermopower was determined from a slope obtained by a plot of the Seebeck voltage versus the temperature gradient.

The density was found to be greater than 95% of the theoretical density for all the samples. X-ray analysis of the samples showed that the β to γ phase transformation is accelerated by the Ti additive. For samples with 0–2 wt % Ti, the major phase was identified as the β phase. In contrast, the sample with 8 wt % Ti consists almost of the γ phase. The samples with 3–7 wt % Ti consist of the β and γ phases. Scanning electron microscopy revealed the dispersion of Ti additives at grain boundaries.[11] By using electron micro-

[a]Author to whom correspondence should be addressed; electronic mail: ohtam@mmm.muroran-it.ac.jp

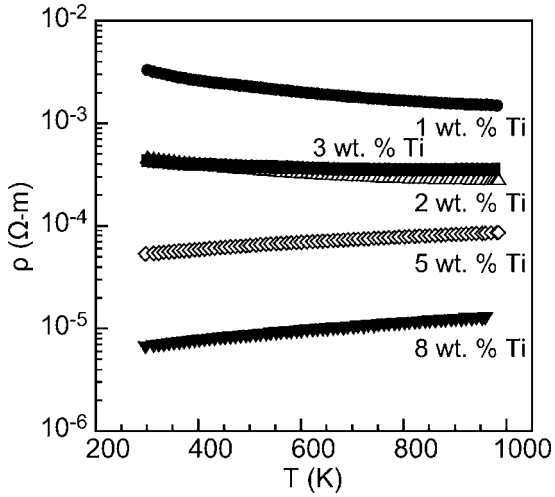

FIG. 1. Temperature dependence of the electrical resistivity for the samples with Ti.

probe analysis, we found that the composition change of the surrounding of Ti promotes the formation of the γ phase.[11] The composition of formed γ phase is nearly $La_2S_{2.67}$.

Figure 1 shows the temperature dependence of the electrical resistivity for the samples with Ti. For the samples with Ti, the heating curves agree with the cooling curves. In contrast, the difference between heating and cooling curves was observed for the pure β phase (with 0 wt % Ti) sample. The electrical properties are changed dramatically through heat treatment. It seems that the β phase is stabilized by the addition of Ti. For the samples with 1–3 wt % Ti, the electrical resistivity decreases with increasing temperature, like an insulator. On the other hand, for the samples with 5–8 wt % Ti, the electrical resistivity increases linearly with increasing temperature. This metallic behavior is attributed to the character of the γ phase.

As shown in Fig. 2, the negative sign of thermopower demonstrates the dominant *n*-type character of all the samples. While the magnitude of thermopower of the β phase with 1 wt % Ti shows a maximum at 600 K, that of the γ phase with 8 wt % Ti increases almost linearly with increasing temperature.

The thermal conductivity is plotted as a function of temperature in Fig. 3. The thermal conductivity κ is given by the

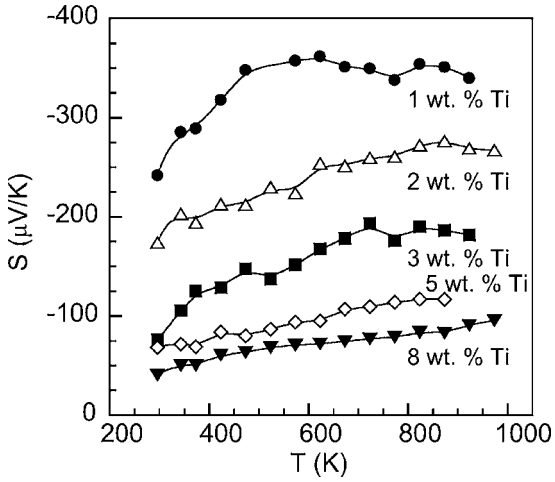

FIG. 2. Temperature dependence of the thermopower for the samples with Ti.

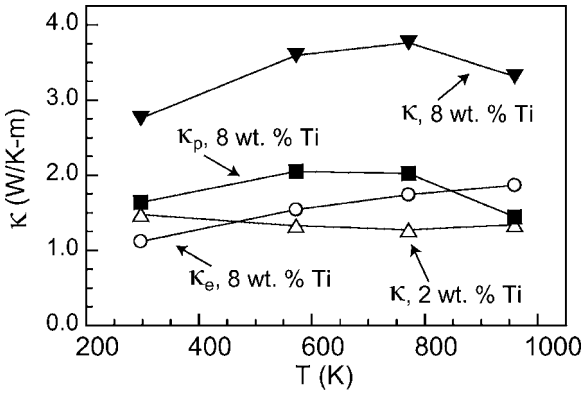

FIG. 3. Temperature dependence of the thermal conductivity for the samples with Ti.

sum of the phonon κ_p and electronic contributions κ_e. Furthermore, the electrical contribution and electrical resistivity are connected through the Wiedemann–Franz law: $\kappa_e\rho = LT$, where L is the Lorenz number (2.45×10^{-8} WΩ/K^2). For the γ phase with 8 wt % Ti, the thermal conductivity is governed by both the phonon and electronic contributions between 300 and 1000 K. On the other hand, the thermal conductivity of the β phase with 2 wt % Ti is governed by phonon contribution, because of its high electrical resistivity. Their phonon contributions are in rough agreement with each other.

The ZT value was calculated from the measured electrical resistivity, thermopower, and thermal conductivity. In γ phase with 8 wt % Ti, the ZT value increases with increasing temperature, reaching a value of 0.21 at 1000 K. Moreover, we found that the β phase with Ti is a candidate material for high-temperature thermoelectric conversion. As temperature increases, the electrical resistivity decreases while the magnitude of the thermopower increases. Consequently, the ZT value increases abruptly from 0.013 at 300 K to 0.18 at 1000 K. As mentioned above, the formation of the β phase degrades the thermoelectric performance of γ phase after the extended heating.[9] However, the high ZT of the β phase can be achieved by the addition of Ti.

The thermoelectric properties of the γ phase with Ti are very similar to that of the degenerate semiconductor γ phase.[1–3] While the Ti additive promotes the formation of the γ phase, it has no effect on the thermoelectric properties. Therefore, the Ti additive is suitable for improving the thermoelectric properties of the γ phase. The control of ratio of La to S is necessary for a further improvement. We believe that the ratio can be controlled by the particle size of Ti additive and the sintering parameters.

In contrast, the insulator-like behavior in electrical resistivity is dominant in the β phase with Ti. The transport mechanism can be well explained by the model of the Anderson localization. We believe that the localized state is caused by the random distribution of oxygen atoms. At high temperature, the transport mechanism is dominated by the excitation from the Fermi level E_C to the mobility edge E_F. The electrical resistivity and thermopower are proportional to $\exp[(E_C - E_F)/k_BT]$ and $1/T$ respectively, where k_B is the Boltzmann constant.[13] As shown in Fig. 4, the high-temperature electrical resistivity follows the theory of the excitation in the Anderson localization. The activation energy $(E_C - E_F)$ decreases as the Ti content increases. This is most likely attributed to the change of oxygen content due to

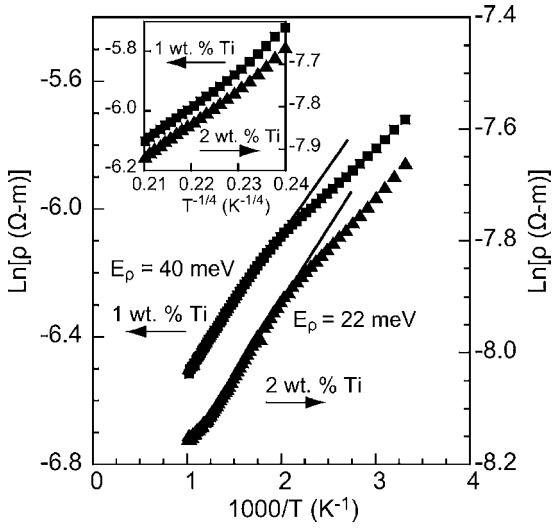

FIG. 4. Arrhenius plots of the electrical resistivity for the β-phase samples with Ti. Inset shows the low-temperature electrical resistivity vs $T^{-1/4}$.

the Ti content and a trace formation of the γ phase. The drop in the magnitude of thermopower for the β phase with 1 wt % Ti above 600 K suggests excitation to the mobility edge, as shown in Fig. 2. The inset of Fig. 4 shows the results of electrical resistivity measurements in the temperature range from 300 to 573 K. At low temperature, the electrical resistivity due to variable range hopping has temperature dependence $[\exp(1/T^{1/4})]$.[13] Indeed, the low-temperature electrical resistivity shows a well-defined $T^{-1/4}$ dependence. If the density of states at Fermi level is not a rapidly varying function of the temperature, the magnitude of thermopower in this regime is proportional to $T^{1/2}$.[13] In Fig. 2, we confirm that the magnitude of low-temperature thermopower for the β phase with 1–2 wt % Ti increases with increasing temperature.

In conclusion, we found that the Ti additive is suitable for improving the high-temperature thermoelectric properties of lanthanum sulfide. The Ti additive promotes the formation of the γ phase with the high thermoelectric performance. Furthermore, the β phase can be stabilized by a small addition of Ti. Like the γ phase, the β phase is a candidate material for the high-temperature thermoelectric energy conversion. The transport mechanism can be explained in terms of the Anderson localized model.

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