



Enhancement in the thermoelectric performance by Y substitution on SrSi 2

C. S. Lue, M. D. Chou, N. Kaurav, Y. T. Chung, and Y. K. Kuo

Citation: Applied Physics Letters **94**, 192105 (2009); doi: 10.1063/1.3136847 View online: http://dx.doi.org/10.1063/1.3136847 View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/94/19?ver=pdfcov Published by the AIP Publishing

Articles you may be interested in

Hot deformation induced defects and performance enhancement in FeSb2 thermoelectric materials J. Appl. Phys. **114**, 184904 (2013); 10.1063/1.4831668

Intrinsically modified thermoelectric performance of alkaline-earth isovalently substituted [Bi2 AE 2O4][CoO2]y single crystals J. Appl. Phys. **114**, 043705 (2013); 10.1063/1.4816315

Enhancement of thermoelectric performance in strontium titanate by praseodymium substitution J. Appl. Phys. **113**, 053704 (2013); 10.1063/1.4790307

High-temperature thermoelectric properties of the double-perovskite ruthenium oxide (Sr1-x La x)2ErRuO6 J. Appl. Phys. **112**, 073714 (2012); 10.1063/1.4757632

Enhanced thermoelectric figure-of-merit ZT for hole-doped Bi2Sr2Co2O y through Pb substitution J. Appl. Phys. **111**, 103709 (2012); 10.1063/1.4720075

Confidently measure down to 0.01 fA and up to 10 PΩ Keysight B2980A Series Picoammeters/Electrometers

Enhancement in the thermoelectric performance by Y substitution on SrSi₂

C. S. Lue,¹ M. D. Chou,¹ N. Kaurav,² Y. T. Chung,² and Y. K. Kuo^{2,a)} ¹Department of Physics, National Cheng Kung University, Tainan 70101, Taiwan ²Department of Physics, National Dong Hwa University, Hualien 97401, Taiwan

(Received 23 February 2009; accepted 23 April 2009; published online 14 May 2009)

We report the results of the Y substitution in $\text{Sr}_{1-x}Y_x\text{Si}_2$ with $x \le 0.15$ via measuring the temperature-dependent electrical resistivity, thermal conductivity, as well as Seebeck coefficient. Upon substituting Y onto the Sr sites, the electrical resistivity exhibit semiconducting behavior and the room-temperature electrical resistivity tends to reduce for $x \le 0.08$. The thermal conductivity also decreases with increasing the Y content. Moreover, the Seebeck coefficient has a substantial increase and a maximum of about 220 μ V/K at around 80 K has been found for x=0.08. These promising effects lead to a significant enhancement in the thermoelectric performance characterized by the figure-of-merit, *ZT*. A room-temperature *ZT* value of approximately 0.4 is thus achieved for Sr_{0.92}Y_{0.08}Si₂, about one order of magnitude larger than that of stoichiometric SrSi₂. © 2009 *American Institute of Physics*. [DOI: 10.1063/1.3136847]

Silicides with semiconducting or semimetallic characteristics have attracted considerable attention because of their practical applications in electronics and thermoelectrics.^{1–3} It is of particular importance that those silicides are composed of nontoxic and naturally abundant elements in the earth's crust. Recently, SrSi₂ was reported to be a narrow-gap semiconductor with a band gap of 35 meV estimated from the Hall coefficient between 180 and 300 K.⁴ Band structure calculations, 5^{-8} on the other hand, indicated the presence of a sharp pseudogap in the Fermi-level density of states (DOS), suggesting a semimetallic character for SrSi₂. As proposed by Mahan and Sofo,⁹ materials with sharp electronic band features of a few tens of meV from the Fermi level would be promising candidates for developing highly efficient thermoelectrics. As a matter of fact, SrSi2 was reported to have a large Seebeck coefficient (S) of approximately 130 μ V/K at 300 K.¹⁰ However, the thermoelectric performance is hampered by its relative high electrical resistivity (ho $\simeq 1 \text{ m}\Omega \text{ cm}$) and thermal conductivity ($\kappa \simeq 5 \text{ W/m K}$) at room temperature,¹⁰ with respect to the dimensionless figureof-merit $ZT = S^2 T / \rho \kappa$.

In general, the difficulty in achieving good thermoelectric performance is characterized by the need to minimize the electrical resistivity and the thermal conductivity of materials, while enhancing their Seebeck coefficient. The strategy to optimize these parameters usually involves the substitution of different elements to alert the electronic band structures in the vicinity of the Fermi level and to enhance the phonon scattering by introducing crystallographic disorder.¹¹ For the present case of SrSi₂, the application of an external pressure has an effect to reduce the electrical resistivity, as observed by Imai *et al.*¹² This encouraging finding suggested that further improvements of the thermoelectric performance on the SrSi₂-based alloys may be made by substituting elements with a small atomic radius which would induce a positively chemical pressure in the system, similar to the pressure effect. With this motivation, we investigate the effects of the chemical substitution on the thermoelectric properties of $Sr_{1-x}Y_xSi_2(0 \le x \le 0.15)$ as Y has a smaller atomic size than Sr. In addition, the replacement of Sr by Y would cause a band structure modification since Y has one more electron in its valence shell than Sr, providing an opportunity for the proximity of the Fermi level to a sharp peak in the DOS.

Polycrystalline $Sr_{1-x}Y_xSi_2$ samples were prepared by mixing appropriate amounts of elemental metals. Mixture of high-purity elements were placed in a water-cooled copper crucible and then melted several times in an argon arcmelting furnace. An x-ray analysis taken with Cu $K\alpha$ radiation on powder specimens was consistent with the expected $P4_332$ structure.^{13,14} The variation in lattice constant as a function of the Y concentration is shown in Fig. 1. It is clearly seen that the lattice constant gradually decreases with x, indicating that the Sr sites are successfully replaced by Y atoms, according to Vegard's law.

The temperature variation in the electrical resistivity for the $Sr_{1-x}Y_xSi_2$ alloys is illustrated in Fig. 2(a), obtained by a standard dc four-terminal method during warming process. The electrical resistivity of $SrSi_2$ exhibits a semimetallic character, showing weak temperature dependence, in agreement with the prediction by the band structure calculation. On the other hand, $\rho(T)$ exhibits a negative temperature coefficient of resistivity (TCR) for each Y-substituted sample, finding reminiscent of semiconducting behavior. However, other mechanisms such as a variable range hopping (VRH) process could also induce the negative TCR response. To



FIG. 1. (Color online) Lattice constant vs Y concentration in $Sr_{1-x}Y_xSi_2$ as obtained from x-ray diffraction.

^{a)}Electronic mail: ykkuo@mail.ndhu.edu.tw.



FIG. 2. (Color online) (a) Electrical resistivity as a function of temperature for $Sr_{1-x}Y_xSi_2$. (b) Seebeck coefficient vs temperature in $Sr_{1-x}Y_xSi_2$.

examine this scenario, the data of $\rho(T)$ were fitted to the Greaves¹⁵ VRH conduction, where the dc resistivity ρ_{dc} obeys the relationship $\rho_{dc} \propto \sqrt{T} \exp[(T_o/T)^{1/4}]$, with the characteristic constant To inversely propositional to the Fermilevel DOS. The satisfactory fitting suggests that the presence of microstructural inhomogeneity or antisite disorder in $Sr_{1-x}Y_xSi_2$ could be the main source for the observed negative TCR. Moreover, the deduced value of T_{o} initially decreases with increasing the Y concentration and then increases with further adding of more Y content. Such a trend is consistent with the variation in the electrical resistivity, indicative of the reliable interpretation for the electrical transport of $Sr_{1-x}Y_xSi_2$. With these respects, it is not appropriate to classify these Y-doped samples as semiconductors with real band gaps in their Fermi-level DOS. Rather, they should be realized as semimetals with pseudogaps in the vicinity of the Fermi levels. Note that the evolution of the electrical resistivity caused by the chemical substitution is not quite consistent with the case of the pressure effect. It is likely that the Fermi-level band structure of SrSi₂ has been severely changed with varying the Y content, especially for the higher Y concentration. As a matter of fact, employing Y as an electron donor in SrSi2 would modify its electronic band feature.

Figure 2(b) shows the Seebeck coefficient as a function of temperature for the $Sr_{1-x}Y_xSi_2$ alloys. The positive sign of *S* for the stoichiometric compound of $SrSi_2$ implies that the hole-type carriers dominate the heat transport. The roomtemperature *S* value of about 135 $\mu V/K$ is consistent with the previously reported result.¹⁰ For the slightly substituted sample (*x*=0.03), the magnitude of *S* tends to reduce, presumably attributed to the band filling effect, as Y has one more electron in its valence shell than Sr. Upon further substituting Y_1 for $Sr_1(x \ge 0.05)$, the magnitude of *S* becomes to



FIG. 3. (Color online) Temperature dependence of the total thermal conductivity in $\text{Sr}_{1-x}Y_x\text{Si}_2$.

increase and consequently decreases after passing through a highest one for x=0.08. The change in *S* with higher Y amounts indicates the modification of the electronic band structure. In these alloys, the Seebeck coefficient develops a broad maximum, a common feature due to the contribution of the thermally excited electrons across their pseudogaps.

For x=0.03, 0.05, and 0.10, the sign of the low-temperature *S* data is negative accompanied by negative peaks at around 50 K. Such a feature can be qualitatively interpreted in terms of two-carrier conduction mechanism. Accordingly, the total *S* can be expressed as

$$S = \frac{\sigma_n}{\sigma_n + \sigma_p} S_n + \frac{\sigma_p}{\sigma_n + \sigma_p} S_p, \tag{1}$$

where $S_{n,p}$ and $\sigma_{n,p}$ represent the Seebeck coefficients and electrical conductivities for the *n*- and *p*-type carriers, respectively. Since the signs of S_n and S_p are opposite, tuning these quantities could result in a sign change in *S*. For these Y-doped samples, the low-temperature Seebeck coefficients are mainly dominated by the *n*-type carriers. However, with increasing temperature, the intrinsic electrons and holes are excited across the pseudogaps. If the holes have a slightly higher mobility than the electrons, the thermal transport is increasingly governed by the *p*-type carriers, as we observed in these materials.

In Fig. 3, we display the observed thermal conductivity for all studied samples. At low temperatures, κ increases with temperature and a maximum appears between 20 and 40 K. This is a typical feature for the reduction in thermal scattering in solids at low temperatures. A remarkable trend found in κ is that the height of the low-temperature peak decreases drastically with increasing the substitution level, indicative of a strong enhancement in the phonon scattering by lattice imperfections. On the other hand, the thermal conductivity exhibits a marginal reduction with the substitution level for $T \ge 200$ K, showing a room-temperature κ of about 5 W/mK. This is attributed to the dominant lattice thermal conductivity (κ_L) to the total κ , as analyzed by Hashimoto *et al.*¹⁰ for SrSi₂₁. The absence of an effective decrease in κ_{rd} to P



FIG. 4. (Color online) ZT value as a function of temperature for $Sr_{1-x}Y_xSi_2$.

is associated with the weak mass fluctuation between Sr and Y, since their mass difference is only about 1%. The results imply that a further reduction in κ is possible if large atomic mass fluctuation is present by alloying heavier elements in SrSi₂.

Figure 4 shows ZT as a function of temperature for $Sr_{1-x}Y_xSi_2$. Remarkably, the $Sr_{0.92}Y_{0.08}Si_2$ specimen has the highest ZT=0.41 at room temperature. This is mainly due to the fact that both ρ and S are optimized with this concentration, although no significant reduction in κ is achieved. This result can be ascribed by the simultaneous presence of the sharp Fermi-level band edge as well as the high mobility of the carriers for this composition. While the highest ZT value among the studied compositions is a bit smaller than that of the optimized Bi₂Te₃($ZT \approx 0.87$),¹⁶ it is comparable to the nonoptimized Bi_2Te_3 having $ZT \simeq 0.55$. Furthermore, $Sr_{0.92}Y_{0.08}Si_2$ shows $S \simeq 135$ V/K and $\rho \simeq 0.28$ m Ω cm at room temperature, resulting in a high thermoelectric power factor $S^2/\rho \simeq 6.5 \times 10^{-3}$ W/m K². This value is larger than those of the thermoelectric materials such as Bi2Te3, $K_2Bi_8Se_{13}$, $CoSi_{1-x}Ge_x$, ^{16–18} and even comparable to that achieved by pressurizing Bi_2Te_3 .¹⁹ It is apparent that the thermoelectric power factor of $Sr_{1-x}Y_xSi_2$ is indeed enhanced with a suitable dopant level. However, the necessary reduction in κ_L should be further improved to enlarge the ZT value.

An extensive investigation of the effect of Y doping in $Sr_{1-x}Y_xSi_2$ is presented via the thermoelectric measurements as a function of temperature. We clearly demonstrate that the Y substitution represents a good opportunity for improving its *ZT*, making this system attractive for possible candidates for low-and intermediate-temperature thermoelectric applications. Small amounts of Y dramatically affect the electronic band structure, and thus the electrical transport properties of these materials. However, one of the challenges which still remain is to reduce the lattice thermal conductivity. Efforts to utilize the mass fluctuation scattering to lower κ are being employed.

This work was supported by National Science Council, Taiwan under Grant Nos. 97-2628-M-259-001-MY3 (YKK) and NSC-95-2112-M-006-021 (CSL).

- ¹T. M. Tritt, M. Kanatzidis, H. B. Lyon, Jr., and G. Mahan, *Symposium Proceedings of the Materials Research Society* (Materials Research Society, Pittsburgh, 1997), 478.
- ²C. S. Lue, Y.-K. Kuo, C. L. Huang, and W. J. Lai, Phys. Rev. B **69**, 125111 (2004).
- ³Y. K. Kuo, K. M. Sivakumar, S. J. Huang, and C. S. Lue, J. Appl. Phys. **98**, 123510 (2005).
- ⁴M. Imai, T. Naka, T. Furubayashi, H. Abe, T. Nakama, and K. Yagasaki, Appl. Phys. Lett. **86**, 032102 (2005).
- ⁵Y. Imai and A. Watanabe, Intermetallics 10, 333 (2002).
- ⁶Y. Imai and A. Watanabe, Intermetallics 14, 666 (2006).
- ⁷S. Brutti, D. Nguyen Manh, and D. G. Pettifor, Intermetallics **14**, 1472 (2006).
- ⁸M. Imai, T. Naka, H. Abe, and T. Furubayashi, Intermetallics **15**, 956 (2007).
- ⁹G. D. Mahan and J. O. Sofo, Proc. Natl. Acad. Sci. U.S.A. **93**, 7436 (1996).
- ¹⁰K. Hashimoto, K. Kurosaki, Y. Imamura, H. Muta, and S. Yamanaka, J. Appl. Phys. **102**, 063703 (2007).
- ¹¹F. J. DiSalvo, Science **285**, 703 (1999).
- ¹²M. Imai, T. Naka, H. Abe, and T. Furubayashi, Intermetallics **15**, 956 (2007).
- ¹³J. Evers, J. Solid State Chem. **24**, 199 (1978).
- ¹⁴M. Imai and T. Kikegawa, Chem. Mater. **15**, 2543 (2003).
- ¹⁵G. N. Greaves, J. Non-Cryst. Solids 11, 427 (1973).
- ¹⁶H. Scherrer and S. Scherrer, in *CRC Handbook of Thermoelectrics*, edited by D. M. Rowe (CRC, Boca Raton, FL, 1995), p. 211.
- ¹⁷D.-Y. Chung, K.-S. Choi, L. Iordanidis, J. L. Schindler, P. W. Brazis, C. R. Kannewurf, B. Chen, S. Hu, C. Uher, and M. G. Kanatzidis, Chem. Mater. 9, 3060 (1997).
- ¹⁸E. Skoug, C. Zhou, Y. Pei, and D. T. Morelli, Appl. Phys. Lett. **94**, 022115 (2009).
- ¹⁹S. V. Ovsyannikov, V. V. Shchennikov, G. V. Vorontsov, A. Y. Manakov, A. Y. Likhacheva, and V. A. Kulbachinskii, J. Appl. Phys. **104**, 053713 (2008).