論 文 の 内 容 の 要 旨

Research for Thermoelectric Properties of Sr_2Si and Ca_2Si

(Sr_2SiとCa_2Siの熱電特性に関する研究)

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Silicides are attractive semiconductors because of their environmental friendliness and their application in electronic and thermoelectric (TE) devices. New and less investigated silicides can replace toxic and expensive transition metal silicides. Within the group of alkaline earth silicides, Mg_2Si has been well studied. An excellent dimensionless figure of merit ($ZT=S^2\sigma\mathrm{T}/\kappa$) of 1.45 at 800 K has been reported. The κ of undoped Mg_2Si remains high (ca. 10 W/m K). However, the κ of undoped Ca_2Si, $SrSi_2$, and $BaSi_2$ at room temperature were 2.31 W/mK, 5.25 W/mK, and 1.56 W/mK, respectively. Experimental evaluation of thermoelectric properties of Ca, Sr, and Ba silicides are lacking, possibly because of the difficulty in synthesis and the high reactivity of the product.

MgSrSi-type (anti-$PbCl_2$ type) structure is an orthorhombic structure of space group Pnma. These compounds including Sr_2Si and Ca_2Si are calculated to be narrow-gap semiconductors, when the number of valence electrons are 8. Among such compounds, we selected Sr_2Si and Ca_2Si due to : 1) relatively wide calculated band gap of ~0.40-0.51 eV, and ~0.35-0.36 eV, Sr_2Si and Ca_2Si, respectively, 2) first-principal calculations predicted high ZT, 3) lower thermal conductivity due to complex crystal structure, 4) raw materials Sr, Ca, and Si are non-toxic and highly earth abundant. Sr_2Si and Ca_2Si have identical band structures, and were calculated to be direct

semiconductors. Although Ca_2Si is predicted to be high ZT material, reported ZT was 2×10^{-5} at 373 K, major reason for lower ZT was high electrical resistivity due to low density.

A suitable type, amount, and distribution of nano- or microsize secondary phase can play an important role in improving the TE properties of composites. The effects of the composite are mainly derived from two phenomena. The first effect is the scattering of phonons by the grain boundary, which also exist in polycrystals of the single phase. Although the mean free path of electrons is mostly shorter than several nm, which is usually smaller than the grain size, that of phonons is widely distributed to more than 1 μm. Therefore, by introducing a grain boundary, the lattice thermal conductivity, κ_{lat}, decreases much more markedly than does the electronic thermal conductivity, κ_{el}, and the electrical conductivity, $\sigma = 1/\rho$, where $\kappa=\kappa_{lat}+\kappa_{el}$. As a result, ZT can be increased. The second effect is precipitate of more conductive phases, such as a metallic phase. In such cases, both ρ and S decrease and S^2/ρ can be optimized as with carrier doping. The second effect should coexist with the first effect. In many cases, these composite effects are used in combination with carrier control effects and can be very effective in increasing ZT.

In this study, we investigated the TE properties of Sr_2Si and Ca_2Si and their composites for mid-temperature applications. Composite effect was used to improve ZT of Sr_2Si and Ca_2Si. We successfully synthesized Sr_2Si and Ca_2Si by the reaction of Sr + $SrSi_2$ and Ca + Si, respectively, in sealed titanium tubes to reduce the vaporization of Sr and Ca, and oxidation of $SrSi_2$ and Si. Secondary phase Sr_5Si_3 and Ca_5Si_3 was introduced into the Sr_2Si and Ca_2Si polycrystalline bulk by partial decomposition during spark plasma sintering (SPS). We evaluated the TE properties of these bulks and investigated their relationship to the microscale distribution of metallic Sr_5Si_3 (Ca_5Si_3) and semiconducting Sr_3SiO (Ca_3SiO) phases. Possible origins of the low thermal conductivity in Sr_2Si and Ca_2Si were also investigated. To the best of our knowledge, we are reporting TE properties of Sr_2Si for the first time. Also, there are only three reported study on TE properties of Ca_2Si.

Nearly single-phase Sr_2Si, and Ca_2Si powder were synthesized with minor amounts of Sr_3SiO and Ca_3SiO phases. Composite samples were obtained through spark-plasma sintering. XRD peaks of Sr_2Si and Ca_2Si are less sharp after SPS compared to their powder samples, which indicates may be cystallinity is lower in them which may cause by unidirectional pressure during SPS. Samples prepared at longer time and higher temperature during SPS showed sharper XRD peaks than samples prepared at lower SPS temperature, for both Sr_2Si and Ca_2Si, indicating better cystallinity. Samples prepared at longer time and higher temperature during SPS showed lower electrical resistivity and higher Seebeck coefficient than samples prepared at shorter time and lower temperature during SPS, for both Sr_2Si and Ca_2Si, may be due to better crystallinity. Microstructural analysis demonstrated that Sr_2Si grains were surrounded by a mixture of smaller grains of Sr_2Si, Sr_5Si_3, and Sr_3SiO in Sr_2Si composite samples. Similarly, Ca_2Si grains were surrounded by a mixture of smaller grains of Ca_2Si, Ca_5Si_3, and Ca_3SiO in Ca_2Si composite samples. Reduction in the electrical resistivity was remarkable by the presence of metallic Sr_5Si_3 and Ca_5Si_3 phases, and it decreased with an increased amount of Sr_5Si_3 and Ca_5Si_3. However, the positive Seebeck coefficient increased with an increased amount of Sr_5Si_3 and Ca_5Si_3. Some of the reasons of higher ρ in Sr_2Si and Ca_2Si can be (i) lower carrier concentration, (ii) oxide phase impurity, and (iii) lower crystallinity. One of the reason of the lower S in Sr_2Si and Ca_2Si can be lower crystallinity. The reasons of higher S in composite samples can be due to (i) decreasing hole carrier concentration, (ii) energy filtering effect, and (iii) increase in crystallinity. The thermal conductivities (lattice thermal conductivity was dominant) were largely unaffected by the presence of either metallic (Sr_5Si_3, Ca_5Si_3) or semiconducting (Sr_3SiO, Ca_3SiO) phase. As a result, the power factor and *ZT* increased with increasing amount of metallic phases. Maximum *ZT* was achieved in those composite samples having the greater amount of Sr_5Si_3 and Ca_5Si_3 phase present.

The electrical resistivity significantly decreased and Seebeck coefficient increased, which is quite different from the conventional composite or carrier control effects. This suggests that there is significant potential for enhancing *ZT* in Sr_2Si-Sr_5Si_3, and Ca_2Si-Ca_5Si_3 composites. The lattice thermal conductivity of the Sr_2Si and Ca_2Si phases was among the lowest of known typical silicides. Lattice thermal conductivity of Sr_2Si and Sr_5Si_3 were consistent with the formula proposed by Slack, but Ca_2Si and Ca_5Si_3 samples slightly deviated. In comparison to previous reports, Ca_2Si samples produced in this work possesses higher density, significantly lower electrical resistivity, and lower thermal conductivity. Due to nearly similar band structures, Sr_2Si and Ca_2Si showed similar composite effect and TE properties.