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Effect of Composition on Thermoelectric Properties of Polycrystalline $CrSi_2$

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Ingots with compositions $CrSi_{2-x}$ (with $0 < x < 0.1$) were synthesized by vacuum arc melting followed by uniaxial hot pressing for densification. This paper reports the temperature and composition dependence of the electrical resistivity, Seebeck coefficient, and thermal conductivity of $CrSi_{2-x}$ samples in the temperature range of 300 K to 800 K. The silicon-deficient samples exhibited substantial reductions in resistivity and Seebeck coefficient over the measured temperature range due to the formation of metallic secondary CrSi phase embedded in the $CrSi_2$ matrix phase. The thermal conductivity was seen to exhibit a U-shaped curve with respect to x, exhibiting a minimum value at the composition of $x = 0.04$. However, the limit of the homogeneity range of $CrSi_2$ suppresses any further decrease of the lattice thermal conductivity. As a consequence, the maximum figure of merit of $ZT = 0.1$ is obtained at 650 K for $CrSi_{1.98}$.

Key words: Thermoelectric materials, chromium disilicide, intermetallics

INTRODUCTION

Transition-metal (TM) silicides have attracted attention for high-temperature thermoelectric applications and Si-based microelectronics due to their thermal and structural stability, high electrical conductivity and thermoelectric power at elevated temperature, and the natural abundance of their constituent elements.[1,2] The usefulness of thermoelectric materials can be determined by a dimensionless performance index called the figure of merit $ZT = S^2T/\kappa\rho$, where S, ρ, κ, and T are the Seebeck coefficient, electrical resistivity, thermal conductivity, and absolute temperature, respectively.

Chromium disilicide ($CrSi_2$) is regarded as a potential p-type thermoelectric (TE) material for high-temperature applications because it exhibits very high-temperature oxidation resistance up to 1000°C and $ZT = 0.25$ parallel to the c-axis, whereas $ZT = 0.07$ in the direction perpendicular to the c-axis,[2] which is limited by a slightly high thermal conductivity (10 W/mK).[3] $CrSi_2$ is a degenerate,[4–6] indirect-band-gap[7,8] (0.35 eV) semiconducting material. It has a hexagonal crystal structure (lattice parameters $a = 4.4281$ Å, $c = 6.3691$ Å) with space group $P6_222$, and band-structure calculations also confirm that $CrSi_2$ is a narrow-gap semiconductor with band gap of 0.30 eV, showing good agreement with experimental values reported in the literature.[9–11]

According to the Cr-Si phase diagram,[12] $CrSi_2$ exhibits a narrow homogeneity range. Change in the composition of $CrSi_2$ should lead to corresponding variation in S, ρ, and κ due to change in the carrier concentration (n) and energy band gap (E_g) and by the created defects. Furthermore, as the percentage Si concentration in $CrSi_2$ either increases or decreases beyond the solubility range, formation of secondary phases of Si or metallic CrSi will result, respectively. The secondary metallic CrSi phase has thermal conductivity of ~12 W/m K, which is slightly higher than that of pure semiconducting $CrSi_2$.[13] In this work, an attempt was made to search for the optimum composition in the range

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