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Thermoelectric properties of the Cu_2SnSe_3–Cu_2GeSe_3 solid solution

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ABSTRACT

We present results on the electrical resistivity, Seebeck coefficient, and thermal conductivity for $Cu_2Sn_{1-x}Ge_xSe_3$ alloys, with x ranging from 0 to 0.5. Samples quenched in water from high temperature were found to crystallize in a disordered zincblende-like structure while samples cooled slowly assumed a monoclinic structure. We observed little phonon scattering due to atomic mass fluctuations upon the addition of Ge at room temperature. The thermal conductivity is analyzed using the Debye model with the Grüneisen constant as the only adjustable parameter. An increase in electrical resistivity for the Ge-containing samples was offset by their enhanced Seebeck coefficients. The slow-cooled $x = 0.2$ sample showed the best thermoelectric properties with dimensionless figure of merit $ZT = 0.0353$ at 300 K, a relatively large value compared to other Cu-based multinary compounds.

1. Introduction

Thermoelectric materials are capable of converting directly between thermal and electrical energy, and thus lend themselves to applications such as waste heat recovery and solid-state cooling. The widespread use of thermoelectric devices has been largely frustrated by their low efficiency, and as a result the search for high-efficiency thermoelectric materials is ongoing. The conversion efficiency of a thermoelectric material is determined by the thermoelectric figure of merit, Z, defined as $Z = \alpha^2\sigma/\kappa$, where α is the Seebeck coefficient, σ the electrical conductivity, and κ the thermal conductivity. Since the units of Z are inverse temperature, it is typically expressed as the dimensionless figure of merit ZT, where T is the absolute temperature. Conventional thermoelectric materials such as Bi_2Te_3 and PbTe can achieve a ZT of less than unity, and the introduction of material with ZT near 2 would represent a substantial increase in efficiency.

Although binary semiconductors have been studied quite extensively as thermoelectric materials, the multitude of ternary semiconducting compounds has seen comparatively less exploration. Ternary compounds of interest can be “built up” from group IV semiconductors via successive isoelectronic substitutions. Early investigations into this approach focused on the bonding nature and structural characterization of such compounds [1,2], and more recent studies have pinpointed compounds of interest for thermoelectric applications such as $AgSbTe_2$ [3,4]. $AgSbTe_2$ belongs to the class of I–V–VI_2 semiconductors which are derived from PbTe by considering two PbTe unit cells (IV_2–VI_2) and replacing the divalent Pb atoms with monovalent group I and trivalent group V atoms. Several I–V–VI_2 compounds are known to maintain the rocksalt crystal structure, giving rise to a high degree of anharmonicity in the octahedrally bonded lattice and thus an intrinsically limited lattice thermal conductivity [4]. $AgSbTe_2$ has the highest figure of merit of any bulk p-type material, with $ZT = 1.3$ at 720 K [5,6]. One can apply a similar approach based upon the III–V semiconductors, from which are derived the chalcopyrite-type materials of composition II–IV–V_2, e.g., $ZnGeAs_2$. Some of the compounds in this family have fairly high ZT, although As-based compounds present toxicity issues. We take a similar approach in the present work by considering the II–VI semiconductors, from which we derive the I_2–IV–VI_3 ternary compounds. These compounds and their solid solutions have seen primarily structural investigations [7–9] and sparse physical property characterization [10,11]. Here, we present results on the thermoelectric properties of the Sn-rich portion of the Cu_2SnSe_3–Cu_2GeSe_3 system.

2. Experimental

Samples of composition $Cu_2Sn_{1-x}Ge_xSe_3$, with x ranging from 0 to 1, were prepared using a direct fusion technique in evacuated quartz ampoules. The starting materials (Cu 99.99% – Alfa Aesar, Sn 99.99%, Ge 99.99%, Se 99.999% – American Smelting and Refining Company) were heated slowly to 900 °C and held for 12 h before being cooled to room temperature. Cooling was accomplished either by maintaining a constant cooling rate in the furnace or by quenching the ampoule in water to achieve a rapid cooling rate. Structural analysis was performed using a Rigaku Miniflex benchtop X-ray diffraction system with Cu Kα radiation. Samples were pulverized and sieved using a 100-mesh screen before being deposited onto glass slides. X-ray patterns were indexed using the MDI Jade 9.0 software package. Polycrys-

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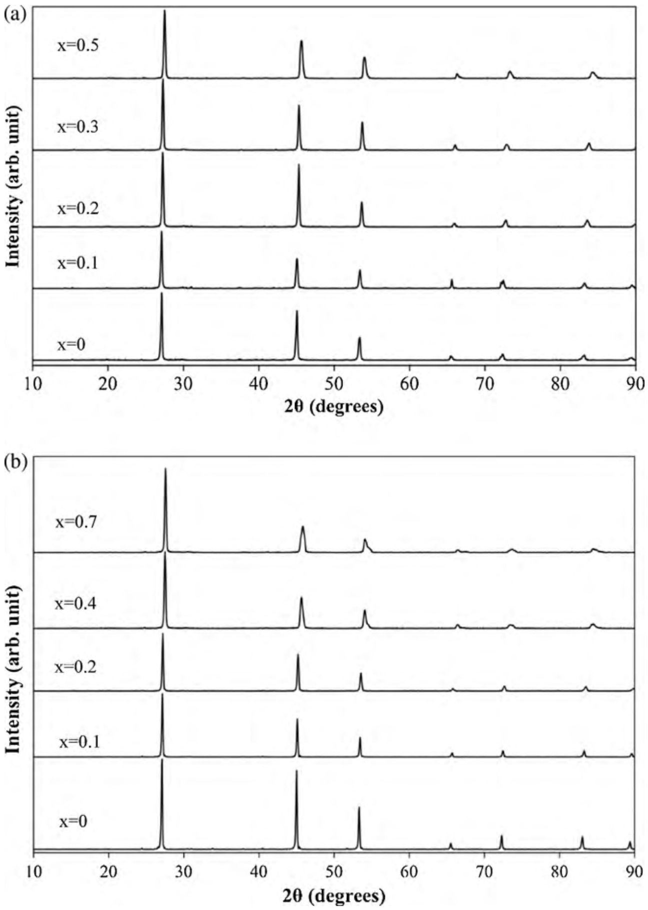

Fig. 1. X-ray powder diffraction patterns for (a) slow-cooled and (b) quenched samples of $Cu_2Sn_{1-x}Ge_xSe_3$ for various values of x shown.

talline samples were cut directly from the ingots as parallelepipeds using a diamond saw, with dimensions of approximately 2 mm × 2 mm ×7 mm. Low-resistance contacts were made to the samples using a silver-filled epoxy. Seebeck coefficient and thermal conductivity measurements were conducted from 80 to 300 K using the standard heater and sink technique in a cryostat with flowing liquid nitrogen as the refrigerant. Electrical resistivity measurements were performed concurrently using a four-probe DC technique. Prior to our measurements, we used a standard fused-quartz sample to calibrate our instrumentation to account for radiation losses. The thermal conductivity data reported in this paper have been corrected based on this calibration. We estimate an uncertainty of ±5% in the thermal conductivity measurements and ±10% in the Seebeck coefficient and electrical resistivity measurements.

3. Results and discussion

Fig. 1 shows X-ray diffraction patterns for both slow-cooled (a) and quenched (b) specimens. Analysis of the X-ray diffraction patterns revealed that slow cooling resulted in a monoclinic structure (space group *Cc* #9) while water quenching resulted in a disordered cubic zincblende-like structure (space group $F\bar{4}3m$ #216). Unit cell dimensions of the monoclinic and cubic phases of Cu_2SnSe_3 can be found elsewhere [7,9]. The quenched samples maintained a cubic structure for $x \le 0.7$, with lattice constants decreasing linearly with x (Fig. 2a), in excellent agreement with those reported by Irie [10]. We found the resulting ingots to be extremely brittle and not suitable for reliable physical property measurements. The slow-cooled samples maintained a monoclinic structure for $x \le 0.5$, above which the orthorhombic structure of Cu_2GeSe_3 was prevalent. The decreasing separation of the (0 0 2) planes with increasing x (Fig. 2b) indicates that Ge successfully substitutes for Sn in the monoclinic structure. The slow-cooled ingots were notably more robust, and were used exclusively for transport property measurements. Multiple samples from each ingot were measured, and certain ingots were found to have charge carrier gradients. Here we present data for representative samples at each composition.

Fig. 3 shows the measured temperature dependence of the Seebeck coefficient. All samples showed increasing thermopower with increasing temperature, reaching a maximum of approximately +210 μV/K for the $x = 0.1$ and $x = 0.2$ samples. The consistently positive values indicate that holes are the majority charge carriers. We expect that a small amount of selenium is lost during synthesis, leading to self-doping and the observed p-type behavior. The Seebeck coefficient increases with increasing x up to $x = 0.2$, and then decreases gradually as x continues to increase.

The measured electrical resistivity is in the range of 4–30 mΩ cm at room temperature, and increases gradually with increasing temperature for the majority of samples (Fig. 4). The $x = 0.1$, 0.2, and 0.3 samples show a slight decrease in resistivity from 80 to 150 K followed by an increase to room temperature. Resistivity does not appear to be dependent on Ge content, which we expect since Ge is substituting isoelectronically for Sn.

The total thermal conductivity (Fig. 5) decreases strongly with increasing temperature for all values of x, indicating that thermal resistance in this regime arises mainly from phonon–phonon interactions. For display purposes Fig. 5 displays data for only the $x = 0$ and $x = 0.5$ samples; the thermal conductivities of the other samples lie in between these two extremes. The electronic component to the thermal conductivity (estimated using the Wiedemann–Franz law) was found to contribute less than 5% of the total for all samples. For comparison we also display the thermal conductivity of ZnSe [12], the "parent" compound to Cu_2SnSe_3. We see that relative to the binary analogue, the thermal conductivity of the ternary compound is nearly an order of magnitude lower. We can understand this behavior by fitting the data to the Debye model. In this model the thermal conductivity can be expressed as [13]

$$\kappa = \frac{k_B^4}{2\pi^2\hbar^3 v} T^3 \int_0^{\theta/T} \frac{x^4 e^x}{(e^x - 1)^2} \tau(x)\, dx \qquad (1)$$

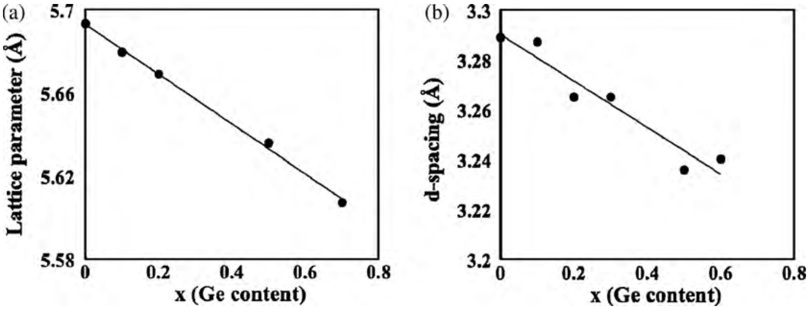

Fig. 2. Variation of the lattice parameter (quenched samples, Fig. 1(a)) and the spacing of the (0 0 2) planes (slow-cooled samples, Fig. 1(b)) with increasing Ge content for the $Cu_2Sn_{1-x}Ge_xSe_3$ compounds.

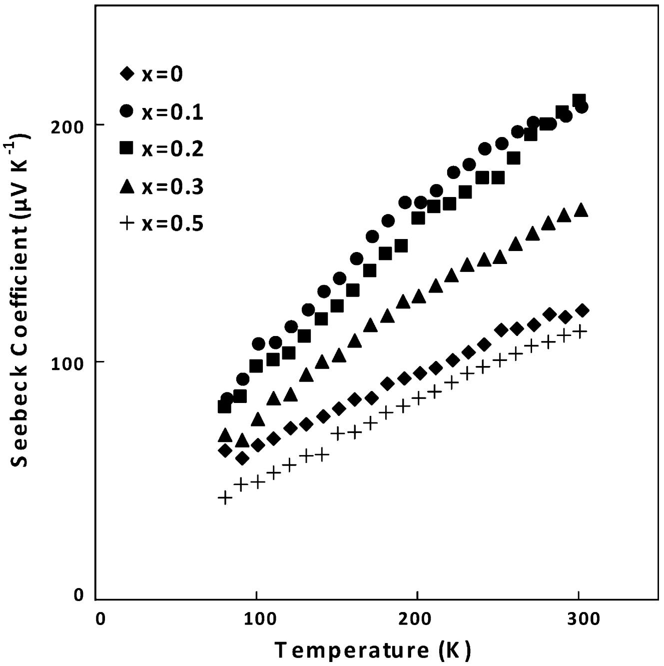

Fig. 3. Temperature dependence of the Seebeck coefficient for the $Cu_2Sn_{1-x}Ge_xSe_3$ compounds.

Here v is the average phonon velocity, θ the average Debye temperature, and $\tau(\omega)$ the scattering time of phonons. As discussed by Slack [14] and Morelli and Slack [15], the appropriate values to use for these parameters are those corresponding to the acoustic part of the phonon spectrum only, as optic modes carry little if any, heat. For ZnSe, the average acoustic mode Debye temperature can be determined directly from the phonon density of states using the procedure described by Slack [14], which yields $\theta = 190$ K. Phonon dispersion curves are not available for Cu_2SnSe_3, so we estimate the average acoustic mode Debye temperature from the Debye temperature determined from the specific heat [16] using the procedure of Slack [14]; this yields $\theta = 93$ K. The average acoustic mode sound velocity is determined by taking the inverse cubic average of the transverse and longitudinal sound velocities [17], which yields $v = 2100\,\mathrm{m\,s^{-1}}$ for ZnSe [18] and $1600\,\mathrm{m\,s^{-1}}$ for Cu_2SnSe_3 [16].

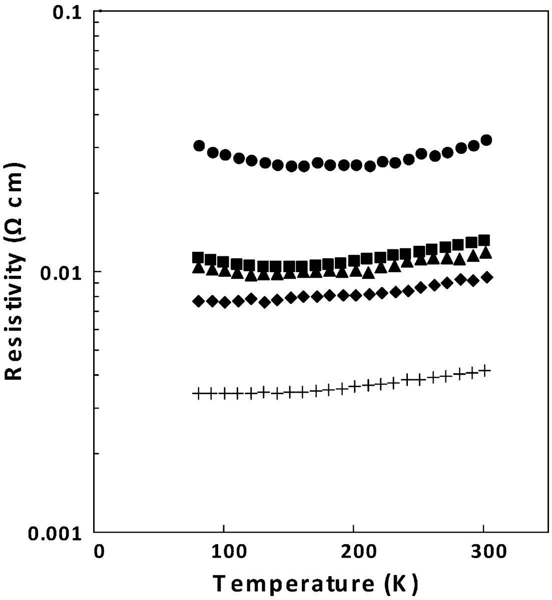

Fig. 4. Temperature dependence of the electrical resistivity for the $Cu_2Sn_{1-x}Ge_xSe_3$ compounds; sample designation as in Fig. 2.

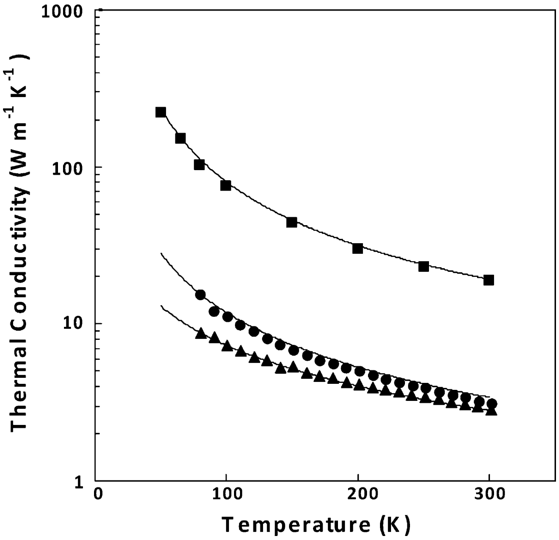

Fig. 5. Temperature dependence of the thermal conductivity for Cu_2SnSe_3 (circles) and $Cu_2Sn_{0.5}Ge_{0.5}Se_3$ (triangles). Also shown are data of Slack for the thermal conductivity of ZnSe (squares). The solid lines are fits to the data using the Debye model described in the text.

The remaining parameter to determine the thermal conductivity using the Debye model is the scattering time $\tau(\omega)$. If we assume that phonon scattering is determined by a combination of grain boundaries, substitutional impurities (in the case of Ge substitution for Sn in Cu_2SnSe_3), and Umklapp processes, the scattering rate is given by

$$\tau^{-1}(x) = \frac{v}{d} + Ax^4T^4 + Bx^2T^3e^{-\theta/3T} \qquad (2)$$

where

$$A = \frac{k_B^4 V\Gamma}{4\pi\hbar^4 v^3} \qquad (3)$$

and

$$B = \frac{\hbar\gamma^2\alpha^2}{Mv^2\theta} \qquad (4)$$

The Umklapp scattering rate and its coefficient B are those given by Slack and Galginaitis [19], and used by Morelli et al. [20] to fit the thermal conductivity of several diamond- and III–V zincblende-structure semiconductors. The parameters V, M, and γ are the average volume per atom, the average atomic mass, and the Grüneisen constant, respectively, d is the grain size (or the sample size for a single crystal) and

$$\Gamma = c\frac{(M - M_{\mathrm{imp}})^2}{M^2} \qquad (5)$$

where M_{imp} is the mass of an impurity atom substituting for M at a concentration c [21].

With this choice of scattering rates the only adjustable parameter is γ. For the case of diamond and III–V zincblende-structure compounds it was found that the γ value so determined was in excellent agreement with values determined from lattice dynamical calculations [20].

To fit the thermal conductivity of the pure ZnSe single crystal, we use the values for θ and v given above and set $d = 1 \times 10^{-3}$ m and $A = 0$. The fit, shown by the solid line in Fig. 5, is excellent and yields a value for the Grüneisen parameter of $\gamma = 1.3$. Talwar et al. [22] provide mode Grüneisen parameters for ZnSe. What we are

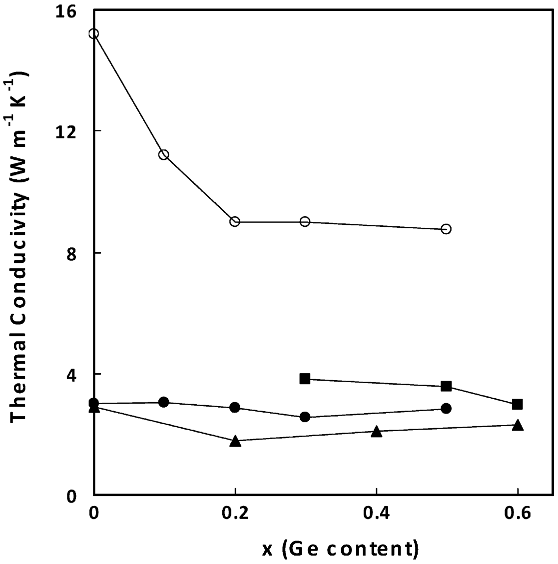

Fig. 6. Thermal conductivity data at 300 K (solid circles) and 80 K (open circles) for the samples studied here. Also shown are data of Averkieva (squares) [7] and Irie (triangles) [10] at 300 K.

interested in here are values of the square root of γ^2 for the acoustic modes, averaged across the entire Brillouin zone [20]. For the longitudinal acoustic mode the Grüneisen parameter is nearly constant at $\gamma \sim 1.2$; the transverse acoustic mode Grüneisen parameter varies strongly and even changes sign across the Brillouin zone, but the average value is approximately 0.75. Thus the value of $\gamma = 1.3$ determined from our fit, which represents an average of all acoustic modes, is very reasonable.

To fit the data on Cu_2SnSe_3, we simply replace v and θ with their values for this compound. Using the same value of γ as that used for ZnSe ($\gamma = 1.3$), we are able to fit the data on this compound almost perfectly; see Fig. 5. Finally, we fit the thermal conductivity of $Cu_2Sn_{0.5}Ge_{0.5}Se_3$ by adding the impurity scattering rate term appropriate to this concentration and mass difference. Here we used the weighted value of the scattering parameter Γ appropriate for a multinary compound following the procedure of Yang et al. [23]. Again, without changing the single adjustable parameter γ, we are able to produce a very high quality fit to the data.

The room temperature value for the thermal conductivity of $Cu2Sn_{1-x}Ge_xSe_3$ remains near 3.0 W/m K over the entire range of x studied here (Fig. 6), indicating that the additional phonon scattering due to the atomic mass difference between Ge and Sn is small relative to intrinsic phonon–phonon scattering in these compounds at 300 K. The data are in reasonable agreement with those of Averkieva et al. [7] and Irie [10] (Fig. 6). Samples measured by Irie were quenched, resulting in a cubic structure, whereas our samples and those measured by Averkieva were slow-cooled, resulting in a monoclinic structure. The partial substitution of Ge for Sn in Cu_2SnSe_3 does, however, result in an approximately twofold decrease in thermal conductivity at liquid nitrogen temperature.

The room temperature thermal conductivities of the $Cu_2Sn_{1-x}Ge_xSe_3$ compounds are significantly lower than that of their parent compound, ZnSe (19 W/m K [12]), and approach those of common thermoelectric materials (PbTe ~ 2.5 W/m K [14], Bi_2Te_3 ~ 1.8 W/m K [24]). Since the thermal conductivity is still decreasing at room temperature, we plan to measure the high-temperature thermal conductivity of these compounds.

4. Conclusions

The low-temperature thermoelectric properties of the Sn-rich $Cu_2Sn_{1-x}Ge_xSe_3$ compounds have been measured. Different cooling rates employed during sample synthesis revealed the high-temperature phase in this system to be disordered zincblende-type and the low-temperature phase to be monoclinic, in agreement with the literature. X-ray diffraction studies showed that Ge successfully substitutes for Sn in both phases.

For the low-temperature monoclinic phase, the optimum thermoelectric properties were observed for the $x = 0.2$ sample, which has $ZT = 0.0353$ at 300 K. This is a modest value, but it is higher than the room temperature figures of merit of other recently reported Cu-based ternary [25] and quaternary [26] compounds.

Acknowledgments

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References

[1] C.H.L. Goodman, R.W. Douglas, Physica (Amsterdam) 20 (1954) 1107.
[2] V.P. Zhuze, V.M. Sergeeva, E.L. Shtrum, Soviet Physics Technical Physics 3 (1958) 10.
[3] V. Jovovic, J.P. Heremans, Physical Review B 77 (2008) 245205.
[4] D.T. Morelli, V. Jovovic, J.P. Heremans, Physical Review Letters 101 (2008) 035901.
[5] C. Wood, Reports on Progress in Physics 51 (1988) 459.
[6] F.D. Rosi, E.F. Hockings, N.E. Lindenblad, RCA Review 22 (1961) 82.
[7] G.K. Averkieva, A.A. Vaipolin, N.A. Goryunova, in: D.N. Nasledov, N.A. Goryunova (Eds.), Soviet Research in New Semiconductor Materials, Consultants Bureau, New York, 1965, p. 26.
[8] B.B. Sharma, H. Singh, Journal of Solid State Chemistry 11 (1974) 285.
[9] G.E. Delgado, A.J. Mora, G. Marcano, C. Rincon, Materials Research Bulletin 38 (2003) 1949.
[10] T. Irie, Japanese Journal of Applied Physics 5 (1966) 854.
[11] G. Marcano, C. Rincon, L.M. de Chalbaud, D.B. Bracho, G. Sanchez Perez, Journal of Applied Physics 90 (2001) 4.
[12] G.A. Slack, Physical Review B 6 (1972) 3791.
[13] R. Berman, Thermal Conduction in Solids, Clarendon Press, Oxford, 1976.
[14] G.A. Slack, Solid State Physics 34 (1979) 1.
[15] D.T. Morelli, G.A. Slack, in: S. Shindé, J.S. Goela (Eds.), High Thermal Conductivity Materials, Springer, New York, 2006, p. 37.
[16] L.I. Berger, Semiconductor Materials, CRC Press, Boca Raton, 1997, p. 260.
[17] N.W. Ashcroft, N.D. Mermin, Solid State Physics, Saunders College, Philadelphia, 1976, p. 457.
[18] B.H. Lee, Journal of Applied Physics 41 (1970) 2988.
[19] G.A. Slack, S. Galginaitis, Physical Review 133 (1964) A253.
[20] D.T. Morelli, J.P. Heremans, G.A. Slack, Physical Review B 66 (2002) 195304.
[21] P.G. Klemens, Proceedings of the Royal Society of London Series A 68 (1955) 1113.
[22] D.N. Talwar, M. Vandevyver, K. Kunc, M. Zigone, Physical Review B 24 (1981) 741.
[23] J. Yang, G.P. Meisner, L. Chen, Applied Physics Letters 85 (2004) 1140.
[24] L. Chen, J. Jiang, X. Shi, Materials Research Society Symposium Proceedings, vol. 793, 2004, p. S9.3.1.
[25] D. Li, X.Y. Qin, Journal of Applied Physics 100 (2006) 023713.
[26] X.Y. Shi, F.Q. Huang, M.L. Liu, L.D. Chen, Applied Physics Letters 94 (2009) 122103.