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Enhanced Thermoelectric Properties of $Ba_xEu_yCo_4Sb_{12}$ with Very High Filling Fraction

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Abstract: Filled skutterudite is one of the most promising thermoelectric materials for power generation applications. We report the high-temperature thermoelectric properties including electrical conductivity, Seebeck coefficient, and thermal conductivity in single-phased polycrystalline dual-element-filled skutterudites $Ba_xEu_yCo_4Sb_{12}$($0<x<0.2$, $0<y<0.3$). The double-filled skutterudites are synthesized by the melting-quenching-annealing method and the bulk pellects are sintered by spark plasma sintering (SPS). High total filling fractions ($x+y>40\%$) with very large power factor of $Ba_xEu_yCo_4Sb_{12}$ over 60 μW/(cm•K^2) at high temperature is obtained. The combination of Ba and Eu fillers inside the voids of the skutterudite structure provides a broad range of resonant phonon scattering and consequently a strong suppression in the lattice thermal conductivity is observed. The lattice thermal conductivity values for $Ba_xEu_yCo_4Sb_{12}$ system are dramatically decreased and the lowest value is about 1.7 W/(m•K) at room temperature. Consequently, enhanced thermoelectric figure of merits (ZT) for Ba and Eu dual-element-filled $CoSb_3$ skutterudites are obtained at elevated temperatures, in particular ZT=1.3 at 850 K for $Ba_{0.19}Eu_{0.23}Co_4Sb_{12}$.

Key words: thermoelectric; filled-skutterudite; transport properties

As one of advanced energy conversion technologies, the application of thermoelectric (TE) power generation has been investigated for several decades[1]. The performance of thermoelectric materials is generally characterized by a dimensionless figure of merit, $ZT=S^2\sigma T/\kappa$, where T is the absolute temperature, S is the Seebeck coefficient, σ is the electrical conductivity, and κ is the thermal conductivity, which is generally a sum of electronic (κ_e) and lattice contributions (κ_L), $\kappa=\kappa_e+\kappa_L$. Thermoelectric performance therefore depends on a balance of the transport properties, which requires high S, high σ, and low κ to achieve high TE performance.

Filled skutterudites have been continuously pursued in the past decade for advanced thermoelectric (TE) applications due to their excellent electrical properties[2-4]. Various elements from alkaline-earths (Ba, Sr, Ca)[5-7], rare-earths (La, Ce, Yb, Eu, Nd)[8-11], alkaline metals (K, Na)[12-13], and a few other atoms (Tl, Sn, Ge)[14-16] have been used as filler atoms to fill into the Sb-icosaedron voids in $CoSb_3$ framework, which have been much investigated to effectively reduce κ_L. The lattice thermal conductivity of the filled skutterudites, however, is still higher than those of many state-of-the-art TE materials, such as Bi_2Te_3[17]. It has been found that different filler atoms have different vibration frequencies in the void of the $CoSb_3$ skutterudites[18]. It has also been demonstrated that filling the voids using more than one type of filler atom could lead to an additional suppression in κ_L in filled-$CoSb_3$[18-21]. The combination of two different filler atoms, such as one alkaline-earth element and one rare-earth element (AE-RE), has been proved to be the most appreciate choice for double-filled $CoSb_3$. The reported ZT values have reached 1.26 (850 K) for $Ba_xCe_yCo_4Sb_{12}$, 1.32 (850 K) for $Sr_xYb_yCo_4Sb_{12}$ and 1.36 (800 K) for $Ba_xYb_yCo_4Sb_{12}$[22-24]. The combination of Eu with Ba is thereby expected to be able to depress the lattice thermal conductivity effectively due to the similar rattling frequency between Eu and Yb in $CoSb_3$. However, there is no report of high-temperature thermoelectric properties on $Ba_xEu_yCo_4Sb_{12}$ compounds yet.

In this paper, a series of polycrystalline dual-element-filled $Ba_xEu_yCo_4Sb_{12}$ and $Ba_xYb_yCo_4Sb_{12}$ samples were synthesized and their high-temperature thermoelectric properties were investigated. The difference on the electrical and thermal transport properties between Ba-Yb and Ba-Eu were also discussed.

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1 Experimental procedure

1.1 Materials

High-purity Ba (99%, shot), Eu (99%, piece), Yb (99%, piece), Co (99.99%, powder) and Sb (99.9999%, shot) metals were used as starting materials.

1.2 Preparation

The stoichiometric constituent elements were mixed according to the nominal composition $Ba_xEu_yCo_4Sb_{12}$ (x=0.2–0.3, y=0.2–0.4) and $Ba_xYb_yCo_4Sb_{12}$(x=0–0.3, y=0–0.2), loaded into carbon crucibles and then sealed in quartz ampoules under vacuum (1×10^{-3} Pa). The quartz ampoules were heated slowly up to 1333–1353 K, soaked for about 4 h and followed by quenching in a water bath. The resulting ingots were annealed at 1030–1050 K for 1–2 w, and then ground into fine powder. The obtained powder was loaded into graphite dies and consolidated by a spark plasma sintering process at 863–883 K for 10 min under a pressure of 50 MPa.

1.3 Characterization

X-ray diffraction (XRD) and electron microprobe analyses (EPMA) show that all the samples are single phased materials having the skutterudite structure with trace amount of oxides. The exact compositions of all samples were determined by EPMA. The electrical conductivity (σ) and Seebeck coefficient (S) were measured by the standard four-probe method (ULVAC-RIKO ZEM-3) in He atmosphere between 300 K and 850 K. The measurements of thermal diffusivity (λ) and specific heat (C_p) were carried out in a flowing Ar atmosphere (Netzsch LFA-427 and DSC 404 C Pegasus, respectively) between 300 K and 850 K. The thermal conductivity (κ) was calculated from the relationship $\kappa=D\lambda C_p$, where D is the mass density. The measured densities of all samples are in the range of 95%–99% of the theoretical values.

2 Result and discussion

Figure 1 and Figure 2 show the temperature-dependent electrical conductivity (σ) and Seebeck coefficient (S) for all samples, respectively. The electrical conductivity (σ) decreases, and the absolute value of Seebeck coefficient (S) increases with increasing temperature. Since Eu, Yb and Ba offer the same free electron to $CoSb_3$, σ increases with increasing the total filling fraction ($x+y$), while S decreases in the whole temperature range. All these show a typical behavior of heavily doped semiconductors.

Figure 3 shows the temperature-dependent power factor ($S^2\sigma$) for all samples. With increasing temperature, the power factors in $Ba_xEu_yCo_4Sb_{12}$ are much greater as compared with those of the single-element-filled skutterudite and $Ba_xYb_yCo_4Sb_{12}$. The maximum power factor for $Ba_{0.19}Eu_{0.23}Co_4Sb_{12}$ reaches 60 μW/(cm•K^2) at 850 K.

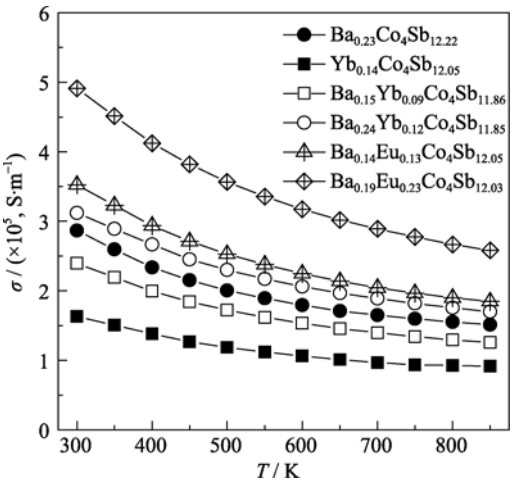

Fig. 1 Measured temperature dependence of the electrical conductivity (σ) in double-filled skutterudites

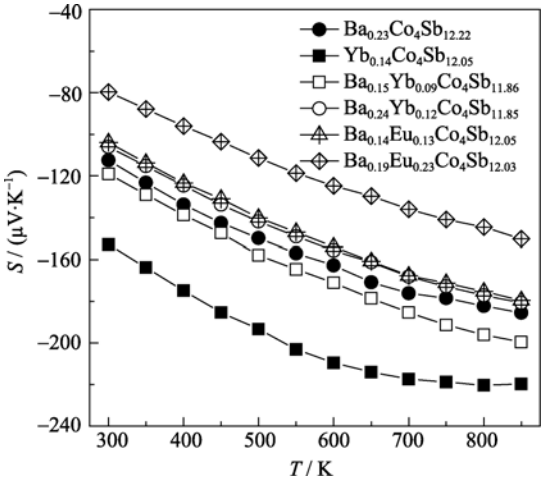

Fig. 2 Measured temperature dependence of the Seebeck coefficient (S) in double-filled skutterudites

Figure 4 and Figure 5 shows the temperature depend-

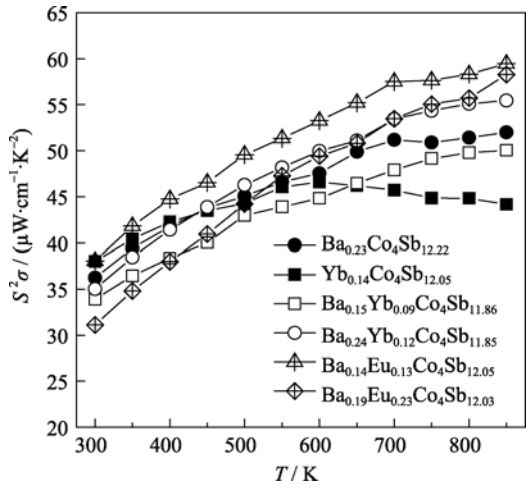

Fig. 3 Measured temperature dependence of the Seebeck coefficient ($S^2\sigma$) in double-filled skutterudites

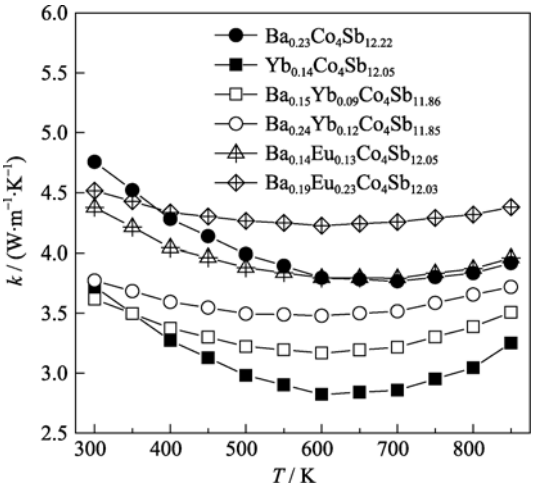

Fig. 4 Measured temperature dependence of total thermal conductivity (κ) in double-filled skutterudites

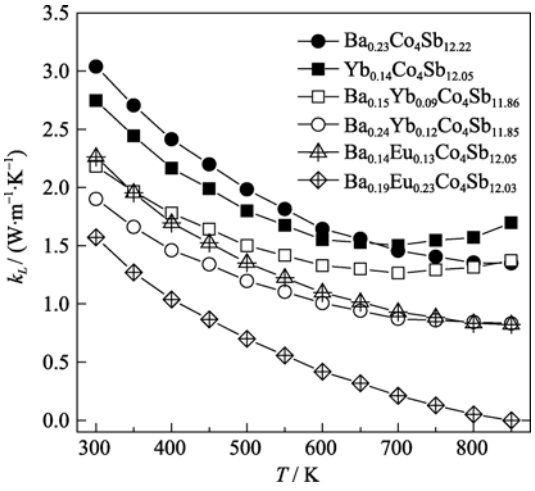

Fig. 5 Measured temperature dependence of lattice thermal conductivity (κ_L) in double-filled skutterudites

ence of total thermal conductivity (κ) and the estimated lattice thermal conductivity ($\kappa_L=\kappa-\kappa_e$) for all samples. The electronic contribution to heat conduction κ_e is calculated using the Wiedemann–Franz law with the Lorenz number equal to 2.45×10^{-8} V^2/K^2. κ_L is obtained by subtracting κ_e from κ. This assessment of κ_L is only an approximation because one does not precisely know the Lorenz number, nor its temperature dependence for this degenerate semiconducting system. Nevertheless, this approach has the virtue of allowing cross-comparisons of existing κ_L values of skutterudites, as it is a common practice to use the Sommerfeld value for the Lorenz number. As compared with Ba or Yb single-element-filled compounds, the κ_L in Ba–Yb and Ba-Eu dual-element-filled $CoSb_3$ compounds is decreased in the whole temperature range. The lattice thermal conductivity of the dual-element-filled $CoSb_3$ decreases with the increase of total filling fraction (x+y). Because the samples have trace amount of oxides, the influence on the lattice thermal conductivity from the oxides can be neglected. With a fixed total filling fraction (x+y) around 0.25, $Ba_{0.14}Eu_{0.13}Co_4Sb_{12}$ and $Ba_{0.15}Yb_{009}Co_4Sb_{12}$ have almost the same κ_L at room temperature, but the κ_L of $Ba_{0.14}Eu_{0.13}Co_4Sb_{12}$ decreases rapidly with increasing temperature and much lower than that of $Ba_{0.15}Yb_{0.09}Co_4Sb_{12}$ at 850 K. Ba-Eu dual-element filling leads to a quickly reduction in κ_L of $CoSb_3$ compared to Ba-Yb double-filled compounds, the κ_L of $Ba_{0.19}Eu_{0.23}Co_4Sb_{12}$ is nearly close to zero above 800 K. The possible reason might be related to the large Lorentz number we used for the calculation of κ_e. The actual Lorentz number in double-filled skutterudites could be much less than the limit value in metals. In this case, the lattice thermal conductivity could be larger than the data shown in Fig. 5.

Figure 6 shows the calculated dimensionless thermoelectric figure of merit as a function of temperature. $Ba_xEu_yCo_4Sb_{12}$ and $Ba_xYb_yCo_4Sb_{12}$ shows enhanced ZT values as compared to Ba or Yb single-filled $CoSb_3$ above 750 K, and their ZTs reach 1.27 at 850 K. In comparison with $Ba_{0.14}Eu_{0.13}Co_4Sb_{12}$, $Ba_{0.19}Eu_{0.23}Co4Sb_{12}$ has similar electrical properties but a slightly higher κ_e, which leads to higher thermal conductivity and lower ZT value in the entire temperature range. This indicates that further enhancement in ZT values for $Ba_xEu_yCo_4Sb_{12}$ compounds could be expected by optimizing the total filling fractions and the ratio of Ba and Eu fillers.

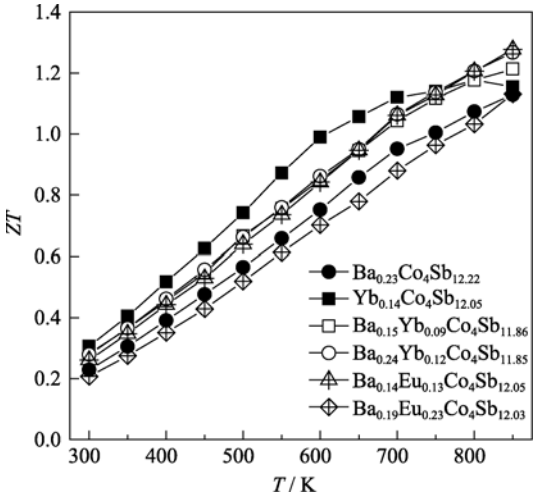

Fig. 6 Measured temperature dependence of dimensionless figure of merit (ZT) in double-filled skutterudites

3 Conclusions

Single-phased polycrystalline dual-element-filled skutterudites $Ba_xEu_yCo_4Sb_{12}$ and $Ba_xYb_yCo_4Sb_{12}$ have been successfully synthesized. Compared to single-filled skutterudites, $Ba_xEu_yCo_4Sb_{12}$ and $Ba_xYb_yCo_4Sb_{12}$ double-filled

skutterudites exhibit similar trend in the electrical transport properties as a function of total filling fraction ($x+y$), suggesting that two-element-double-filling in $CoSb_3$ does not significantly change the characteristics in electrical transports in comparison to the single-element filling. Similar to $Ba_xYb_yCo_4Sb_{12}$ compounds, Ba-Eu co-filling also leads to an additional reduction in lattice thermal conductivity (κ_L) compared to Ba or Yb single-element filling. The enhanced thermoelectric performance is realized in the double-filled $CoSb_3$ systems. The ZT value reaches 1.27 (850 K) for $Ba_{0.14}Eu_{0.13}Co_4Sb_{12}$ and $Ba_{0.24}Yb_{0.12}Co_4Sb_{12}$, but $Ba_{0.19}Eu_{0.23}Co_4Sb_{12}$ possesses a low ZT value because of the high electrical conductivity and thereby high κ_e. Further compositional optimization is expected to get even higher ZT in Ba–Eu co-filled $CoSb_3$.

References:

[1] Slack G A. In: Rowe D M, editor. CRC Handbook of Thermoelectrics. Boca Raton, FL: CRC Press; 1995**:** 407.

[2] Sales B C, Mandrus D, Williams R K. Filled skutterudite antimonides: a new class of thermoelectric materials. *Science*, 1996, **272(5266):**1325–1328.

[3] Sales B C, Mandrus D, Chakoumakos B C, *et al*. Filled skutterudite antimonides: electron crystals and phonon glasses. *Phys. Rev. B*, 1997, **56(23):** 15081–15089.

[4] Nolas G S, Cohn J L, Slack G A. Effect of partial void filling on the lattice thermal conductivity of skutterudites. *Phys. Rev. B*, 1998, **58(1):**164–170.

[5] Chen L D, Karahara T, Tang X F, *et al*. Anomalous barium filling fraction and n-type thermoelectric performance of $BayCo_4Sb_{12}$. *J. Appl. Phy.*, 2001, **90(8):**1864–1868.

[6] Zhao X Y, Shi X, Chen L D, *et al*. Synthesis and thermoelectric properties of Sr-filled skutterudite $Sr_yCo_4Sb_{12}$. *J. Appl. Phy.*, 2006, **99(5):** 053711–1–4.

[7] Puyet M, Lenoir B, Dauscher A, *et al*. High temperature transport properties of partially filled $Ca_xCo_4Sb_{12}$ skutterudites. *J. Appl. Phy.*, 2004, **95(9):** 4852–4855.

[8] Morelli D T, Meisner G P, Chen B X, *et al*. Cerium filling and doping of cobalt triantimonide. *Phys. Rev. B*, 1997, **56(12):** 7376–7383.

[9] Nolas G S, Kaeser M, Littleton V R T, *et al*. High figure of merit in partially filled ytterbium skutterudite materials. *Appl. Phys. Lett.*, 2000, **77(12):**1855–1857.

[10] Lamberton G A, Bhattacharya S, Littleton R T, *et al*. High figure of merit in Eu-filled $CoSb_3$-based skutterudites. *Appl. Phys. Lett.*, 2002, **80(4):** 598–600.

[11] Kuznetsov V L, Kuznetsov L A, Rowe D M. Effect of partial void filling on the transport properties of $Nd_xCo_4Sb_{12}$ skutterudites. *J. Phys.: Condens. Matter*, 2003, **15(29):** 5035–5048.

[12] Pei Y Z, Chen L D, Zhang W, *et al*. Synthesis and thermoelectric properties of $K_yCo_4Sb_{12}$. *Appl. Phys. Lett.*, 2006, **89(22):** 221107–1–3.

[13] Pei Y Z, Yang J, Chen L D, *et al*. Improving thermoelectric performance of caged compounds through light-element filling. *Appl. Phys. Lett.*, 2009, **95(4):** 042101–1–3.

[14] Sales B C, Chakoumakos B C, Mandrus D. Thermoelectric properties of thallium-filled skutterudites. *Phys. Rev. B*, 2000, **61(4):** 2475–2481.

[15] Nolas G S, Takizawa H, Endo E, *et al*. Thermoelectric properties of Sn-filled skutterudites. *Appl. Phys. Lett.*, 2000, **77(10):** 52–54.

[16] Nolas G S, Yang J, Takizawa H. Transport properties of germanium-filled $CoSb_3$. *Appl. Phys. Lett.*, 2004, **84(25):** 5210–5212.

[17] Uher C. In: Tritt T M, editor. Recent Trends in Thermoelectric Materials Research I, Semiconductors and Semimetals. CA: Academic Press, 2000**:**139.

[18] Yang J, Zhang W, Bai S Q, *et al*. Dual-frequency resonant phonon scattering in $Ba_xR_yCo_4Sb_{12}$. *Appl. Phys. Lett.*, 2007, **90(19):** 192111–1–3.

[19] Berardan D, Alleno E, Godart C, *et al*. Improved thermoelectric properties in double-filled $Ce_{y/2}Yb_{y/2}Fe_{4-x}(Co/Ni)_xSb_{12}$ skutterudites. *J. Appl. Phys.*, 2005, **98(3):**033710–1–6.

[20] Lu Q M, Zhang J X, Zhang X, *et al*. Effects of double filling of La and Ce on thermoelectric properties of $Ce_mLa_nFe_{1.0}Co_{3.0}Sb_{12}$ compounds by spark plasma sintering. *J. Appl. Phys.*, 2005, **98:**106107–1–3.

[21] Tang X F, Li H, Zhang Q J, *et al*. Synthesis and thermoelectric properties of double-atom-filled skutterudite compounds Ca_mCe_n-$Fe_xCo_{4-x}Sb_{12}$. *J. Appl. Phys.*, 2006, **100(12):** 123702–1–8.

[22] Bai S Q, Pei Y Z, Chen L D, *et al*. Enhanced thermoelectric performance of dual-element-filled skutterudite $Ba_xCe_yCo_4Sb_{12}$. *Acta Mater. Appl.*, 2009, **57(11):** 3135–3139.

[23] Bai S Q, Shi X, Chen L D. Lattice thermal transport in $Ba_xRE_yCo_4Sb_{12}$(RE=Ce, Yb, and Eu) double-filled skutterudites. *Appl. Phys. Lett.*, 2010, **96(20):** 202102–1–3.

[24] Shi X, Kong H, Uher C, *et al*. Low thermal conductivity and high thermoelectric figure of merit in *n*-type $Ba_xYb_yCo_4Sb_{12}$ double-filled skutterudites. *Appl. Phys. Lett.*, 2008, **92(18):** 182101–1–3.

高填充量 $Ba_xEu_yCo_4Sb_{12}$ 方钴矿热电性能研究

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摘 要: 利用熔融法和等离子放电烧结(SPS)制备单相双原子填充 $Ba_xEu_yCo_4Sb_{12}$ 方钴矿材料并测试其高温热电性能。实验发现, 在高填充量下($x+y$>40%), 材料在高温时具有高的功率因子(>60 W/(cm•K^2))。在方钴矿的晶格空洞中同时引入 Ba 和 Eu 两种填充原子, 能增强晶格声子散射, 从而大幅降低方钴矿的晶格热导。实验证实, $Ba_xEu_yCo_4Sb_{12}$ 体系的晶格热导显著降低, 其室温晶格热导最低达 1.7 W/(m•K)。与此对应的是双原子填充 $Ba_xEu_yCo_4Sb_{12}$ 方钴矿材料的热电优值(ZT 值)明显增大, 其中 $Ba_{0.19}Eu_{0.23}Co_4Sb_{12}$ 的 ZT 值在 850 K 时达到了 1.3。

关 键 词: 热电; 填充方钴矿; 输运性能

中图分类号: TQ174 **文献标识码:** A