

# Thermoelectric Performance for SnSe Hot-Pressed at Different Temperature

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Herein, nanoparticles SnSe are prepared by fusion method together with ball-milling technique and the effect of hot-pressing temperatures on the thermoelectric properties of the dense materials is explored. Due to the optimization of carrier concentration, the peak figure of merit (ZT) value of the compacted material reaches 0.73 for SnSe sample hot-pressed at 400°C and 450°C. The present investigation indicates that the thermoelectric performance of the SnSe compound can be significantly improved by sintering with suitable temperature.

**Key words:** Thermoelectric properties, hot-pressing

## INTRODUCTION

Thermoelectric effects, inter-conversion between heat and electricity, serve as one of the most promising pollution-free ways to ease the growing energy and environmental crisis nowadays.<sup>1</sup> However, it has found only limited applications due to the low conversion efficiency of current thermoelectric materials. The efficiency of thermoelectric materials is defined as the dimensionless figure of merit (ZT), which derives from a combination of three physical properties: thermal conductivity ( $\kappa$ ), electrical conductivity ( $\sigma$ ) and Seebeck coefficient ( $S$ ),  $ZT = S^2\sigma T/\kappa$ , with temperature  $T$ . A good thermoelectric material should have a high power factor ( $PF = S^2\sigma$ ) combined with a low thermal conductivity.

Among the promising thermoelectric materials, SnSe compound has received considerable attention as potential high performance thermoelectric material due to their non-toxicity, environmental friendliness, and abundance of their constituent elements in the earth's crust.<sup>2–3</sup> Very recently, the surprisingly high record  $ZT \approx 2.6$  and  $2.3$  at 923 K along the  $b$  and  $c$ -axis are reported by Zhao et al.<sup>2</sup> in  $p$ -type SnSe single crystal, arising from the

intrinsically ultralow thermal conductivity due to strong anharmonicity of the chemical bonds. A record high average ZT of 1.34, with ZT ranging from 0.7 to 2.0 at 300–773 K, is realized in sodium doped SnSe single crystals.<sup>3</sup> However, due to the long duration of synthesis and the poor mechanical properties for layered single crystalline SnSe, thermoelectric properties of polycrystalline SnSe materials are studied. As one of IV–VI compounds, SnSe with narrow band-gap with layered structure has orthorhombic Pnma space at room temperature. Around 773 K, it undergoes a phase transition from Pnma space to Cmcm space group. Sassi et al.<sup>4</sup> reported the thermoelectric properties of polycrystalline SnSe and obtained the maximum ZT of 0.5 at 820 K. The value was significantly lower than those measured in single crystal SnSe due to higher  $\kappa$  and lower  $\sigma$ . ZT value for  $p$ -type polycrystalline SnSe was enhanced to 1.0 benefiting from texture modulation.<sup>5</sup>

We try to introduce nano-inclusions such as PbTe and carbon black into the matrix SnSe. However, due to the thermoelectric performance for matrix SnSe is not so high ( $<0.6$ ), ZT for these nanocomposite samples only reach 1.26. Hence, to obtain SnSe matrix with high ZT is very important.

Herein, we prepare nano-powder SnSe by fusion method together with ball-milling technique. The

obtained SnSe nanocrystals are hot-pressed into dense materials and the effect of hot-pressing temperatures on the thermoelectric properties of the dense materials is explored. The peak ZT value of the compacted materials reaches 0.73 for SnSe sample hot-pressed at 400°C and 450°C, which is 46% larger than that reported by Sassi et al.<sup>4</sup>

## EXPERIMENTAL PROCEDURE

Elemental Sn (99.99%, Alfa Aesar) and Se (99.999%, Alfa Aesar) powders are weighed according to the formula of SnSe. The powder mixtures are loaded into quartz ampoule sealed under vacuum at  $10^{-3}$  Pa, and then heated to 1223 K over 10 h, soaking at that temperature for 24 h, followed by furnace-cooling to room temperature. The obtained ingot is ground into powder.

Powders of SnSe are hot-pressed into dense pellets at a pressure of 600 MPa at 250°C, 300°C, 350°C, 400°C and 450°C for 1 h. The sintering temperature and heating rate are 673 K and 7 K/min, respectively.

The product is characterized by x-ray diffraction (XRD) using Philips X'Pert PRO x-ray diffractometer equipped with graphite monochromatic Cu K $\alpha$  radiation ( $\lambda = 1.54056$  Å). The operation voltage and current are kept at 40 kV and 40 mA, respectively. The morphology is characterized by field emission scanning electron microscopy (FESEM; SU8020).

For the electrical resistivity and Seebeck coefficient measurements, bar samples of about 2 mm  $\times$  3 mm  $\times$  10 mm are measured using a commercial four-probe apparatus (ULVAC-RIKO ZEM-3). The thermal diffusion  $\lambda$  is obtained by a laser flash method (Netzsch LFA-457) performed on round disk samples with diameters of about 11 mm and thicknesses of about 1.5 mm. The specific heat,  $C_p$ , is determined by differential scanning calorimetry (Netzsch DSC-404C). The thermal conductivity is calculated from  $\kappa = \lambda C_p d$ , where  $d$  is the density of the sample determined by Archimedes' method. The uncertainty for the electrical resistivity is 3%, the Seebeck coefficient 5%, the thermal conductivity 7% (comprising uncertainties of 4% for the thermal diffusivity, 5% for the specific heat, and 3% for the density), so the combined uncertainty for the power factor is 10% and that for ZT value is 12%.

## RESULTS AND DISCUSSION

X-ray diffraction (XRD) patterns for SnSe sample hot-pressed at different temperature are shown in Fig. 1. The main diffraction peaks for bulk SnSe correspond to the standard SnSe phase (Joint Committee on Powder Diffraction Standard (JCPDS) No. 89-0233) with lattice constants  $a = 11.5172$  Å,  $b = 4.1666$  Å,  $c = 4.4402$  Å, no additional peaks are observed for bulk materials compacted from SnSe at hot pressing (HP) temperatures

from 250°C to 450°C, indicating that the specimen has the same crystallographic structure as that of SnSe phase.

Fractographs of SnSe bulk samples hot-pressed from 250°C to 450°C are shown in Fig. 2, one can see that there are many white spots with sizes of approximately 10–50 nm distributed among the big gray grains as shown in Fig. 2a–d. As increasing hot-pressing temperature the number of nanograins reduces. When the hot-pressing temperature increases to 450°C, no nanograins exist in the bulk. By careful inspection with energy dispersive x-ray spectroscopy (EDX) for bulk sample hot-pressed at 400°C, one finds that these areas contain the elements Sn and Se (Fig. 2e) with the ratio of Sn:Se = 1:0.95.

Bar samples with dimensions of about 2 mm  $\times$  3 mm  $\times$  10 mm were cut from the disk samples for measuring the electrical resistivity ( $\rho$ ) and Seebeck coefficients. The electrical resistivity of SnSe nanostructured bulk materials is shown in Fig. 3a. The temperature dependence of electrical resistivity for all the samples hot-pressed at the different temperature is similar, i.e.,  $\rho$  initially decreases as the temperature increases from 300 to 600 K, then  $\rho$  keeps unchanged with further increasing temperature. As the hot-pressing temperature increases from 250°C to 400°C, the electrical resistivity increases in the temperature range of 300–600 K; however,  $\rho$  decreases as HP temperature increases from 400 to 450°C. Specially,  $\rho_{RT}$  increases from 0.00446  $\Omega$  m to 0.01918  $\Omega$  m with increasing HP temperature from 275 to 400°C; then decreases to 0.01212  $\Omega$  m with further increasing HP temperature to 450°C.

Room temperature carrier concentration ( $c$ ) for SnSe is  $1.22 \times 10^{17}$  cm $^{-3}$ ,  $8.68 \times 10^{16}$  cm $^{-3}$ ,  $6.24 \times 10^{16}$  cm $^{-3}$ ,  $5.78 \times 10^{16}$  cm $^{-3}$  and  $5.57 \times 10^{16}$  cm $^{-3}$  sintered at temperature of 250°C, 300°C, 350°C, 400°C and 450°C, respectively. The corresponding carrier mobility is 114.9 cm $^2$  V $^{-1}$  s $^{-1}$ , 65.8 cm $^2$  V $^{-1}$  s $^{-1}$ ,

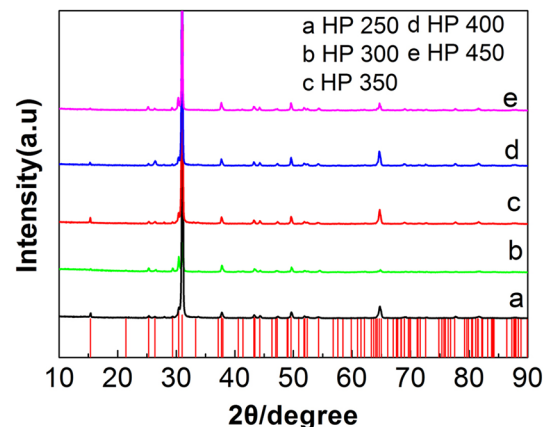


Fig. 1. Bulk XRD patterns for SnSe hot-pressed at different temperature.

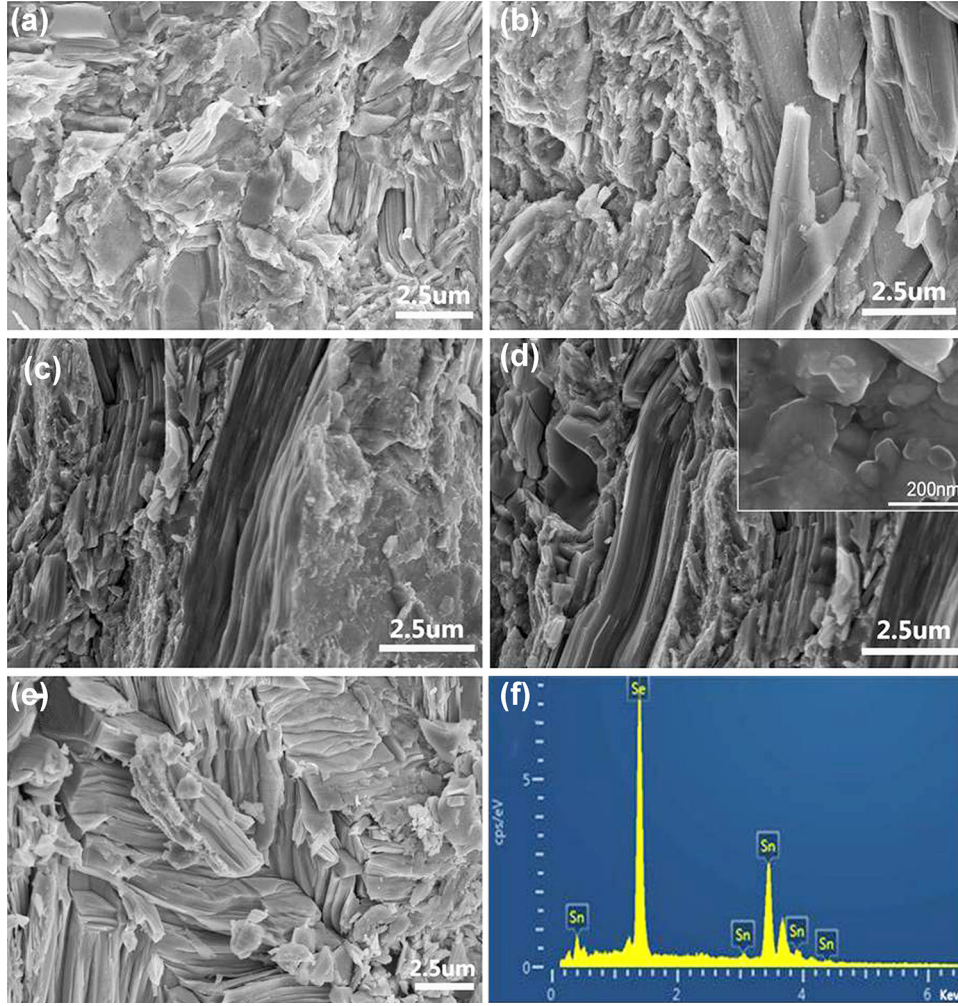


Fig. 2. SEM images of the fractured surface of the bulk sample for SnSe hot-pressed at 400°C (a–e) and EDS spectrum of SnSe (f).

$60.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ,  $56.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and  $92.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ .

The increase in the electrical resistivity with increasing HP temperature may originate from the selenium vacancies in the compacted bulk materials, causing decrease in the carrier concentrations; subsequent decreased  $\rho$  for SnSe hot-pressed at 450°C is mainly attributed to the decreased interface density and pores arising from the grain growth and densification. In addition, a good linear relationship between  $\ln\rho$  and  $1/T$  for SnSe hot-pressed at different HP temperature exists in the high temperature range of 600–775 K, as shown in the inset of Fig. 3a. By using a thermally activated expression in the corresponding temperature regime, written as:

$$\ln\rho = C - \frac{E_g}{2k_B T} \quad (1)$$

where  $C$ ,  $k_B$  and  $E_g$  is a constant, Boltzmann constant and band gap, respectively. From the best fit of the experimental data with formula (1), one

can obtain  $E_g = 0.90 \text{ eV}$ ,  $0.89 \text{ eV}$ ,  $0.95 \text{ eV}$ ,  $0.94 \text{ eV}$  and  $0.96 \text{ eV}$  for SnSe hot-pressed at 250°C, 300°C, 350°C, 400°C, 450°C, respectively, which are almost equal to the energy gap  $E_g = 0.86 \text{ eV}$  for SnSe.<sup>2</sup> This indicates intrinsic excitation is occurred in the temperature range of 600–775 K.

The positive values of the Seebeck coefficient for SnSe determined over the temperature ranging from 300 to 950 K, as shown in Fig. 3b, mean that the major charge carriers for all the samples are holes. The Seebeck coefficient for SnSe hot-pressed at different HP temperature shows a similar temperature behavior: with increasing temperature  $S$  increases in the temperature ranges of 300–400 K and 490–600 K; it decreases in the temperature ranges 400 K–490 K and 600 K–800 K, and above 800 K,  $S$  increases with increasing temperature. The decrease in the Seebeck coefficient in the temperature range of 600 K–800 K for the samples originates from the thermal excitation of the carriers. A pit is observed in the temperature range from 400 to 600 K for SnSe, while this phenomenon is not found for single crystalline samples.<sup>2</sup> The pit may be

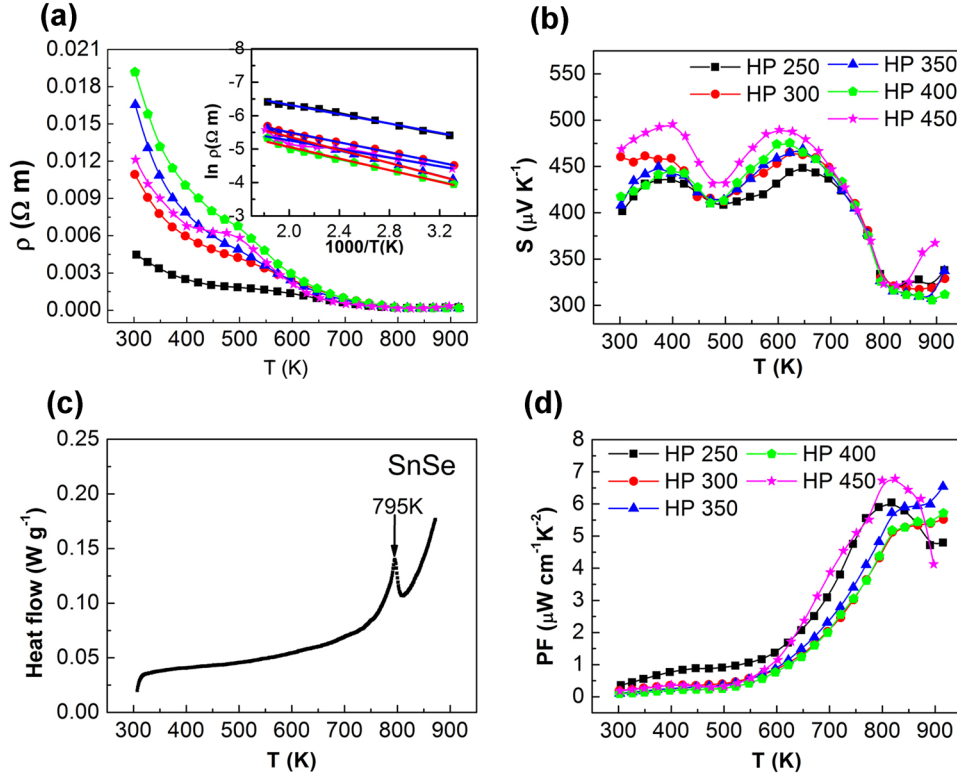


Fig. 3. Temperature dependence of (a) electrical resistivity  $\rho$ , (b) Seebeck coefficient  $S$  and (d) power factor  $PF$  for SnSe hot-pressed at different temperature; (c) DSC curves for SnSe.

due to the contribution of defect levels, which lie close to the edge of valence band, while there are no defect levels in a perfectly crystalized single crystal. The observed anomaly in the  $S$ - $T$  curve above 800 K is associated with a phase transition.<sup>2</sup> DSC analysis shown in Fig. 3c indicates that an endothermic peak  $P$  is located in the temperature range 768–811 K and the peak heat-flow temperature  $T_S$  is at around 795 K. This result is quite consistent with the results reported by Wiedemeier and von Schnering<sup>6</sup> where with increasing temperature, the structure of SnSe is observed to evolve continuously from a layered orthorhombic crystal structure (GeS structure type; space group  $Pnma$ ) into a higher-symmetry variant (TII structure type; space group  $Cmcm$ , No. 63), with a critical temperature of 807 K, indicating that the corresponding anomaly appeared in the  $S$ - $T$  plot is actually composed of two sub-transitions. In general, the trend of the Seebeck coefficient of materials is the same as the electrical resistivity, assuming that electrical properties are strongly correlated with carrier concentration.<sup>7</sup> However, the Seebeck coefficient of SnSe nanostructured bulk materials disagrees with the general trend, implying that other factors such as density of states near the Fermi surface and potential barrier scattering might simultaneously affect the electrical properties along with the carrier concentrations.

Power factor (see Fig. 3d) for SnSe increases with increasing temperature from 300 K to 800 K. Above 800 K, the samples preserve a high power factor. The maximum power factor for SnSe hot-pressed at different HP temperature is between 5.7 and 6.8  $\mu\text{W cm}^{-1} \text{K}^{-2}$ . The peak PF reached 6.8  $\mu\text{W cm}^{-1} \text{K}^{-2}$  for the sample hot-pressed at 450°C for 1 h (observed at 800 K).

The heat capacity ( $C_p$ ) is shown in Fig. 4a. One can see that the heat capacity for SnSe is nearly unchanged with temperature from 300 to 700 K, then it increases rapidly with increasing temperature and decreases suddenly, leaving a peak at about 795 K, then with further increasing temperature it rises. The value of  $C_p$  for our polycrystalline SnSe is between 0.23 and 0.46 J/(g K), which is comparable to the value reported by Sassi et al.<sup>4</sup> The difference is no any abnormality observed around at 500 K in our sample but existed for polycrystalline SnSe reported by Sassi et al.

Considering the anisotropic structure of SnSe, the thermal conductivity of SnSe bulk materials are measured in the same direction as that of electrical properties. The total thermal conductivity  $\kappa$  as a function of temperature for SnSe is given in Fig. 4b. One can see that  $\kappa$  for SnSe first decreases, then rapidly increases and further decreases with increasing temperature. The difference of  $\kappa$  for SnSe hot-pressed at different temperature is small.

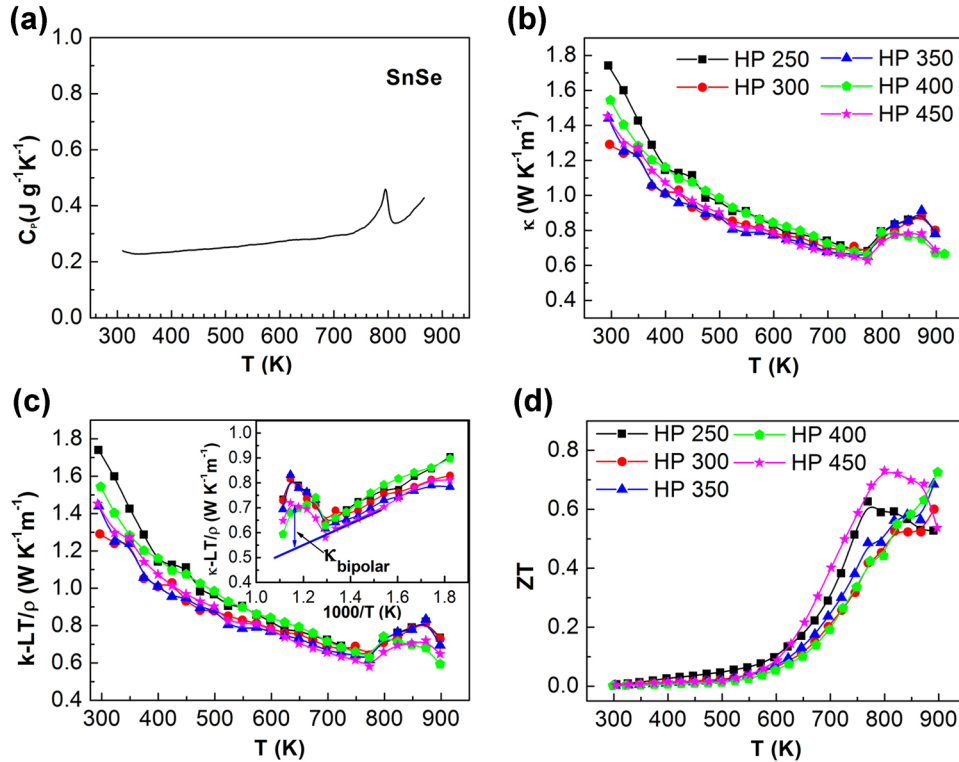


Fig. 4. Heat capacity curve for SnSe (a); temperature dependent (b) thermal conductivity  $\kappa$ , (c)  $\kappa-LT/\rho$ , and (d) figure of merit ZT for SnSe hot-pressed at different temperature.

Subtracting the carrier thermal conductivity ( $\kappa_C$ ), expressed as  $\kappa_C = L_0 T \sigma$  (here  $L_0$  is the Lorenz number ( $1.5 \times 10^{-8} \text{ V}^2 \text{ K}^{-2}$ )), from  $\kappa$ ,  $\kappa-LT/\rho$  can be obtained as shown in Fig. 4c. It can be seen that  $\kappa-LT/\rho$  for SnSe first decreases with increasing temperature because of the phonon-phonon Umklapp scattering (U-scattering). For semiconductors with U-scattering as the dominant phonon scattering mechanism, it is expected that above the Debye temperature ( $\Theta_D \approx 220 \text{ K}$  for SnSe)  $\kappa_L$  should change with  $1/T$ .<sup>8</sup> However,  $\kappa-LT/\rho$  then quickly increases from about 770 K. The portion of the plot around 770 K that deviates from this temperature dependence as shown in the inset of Fig. 4c can be described as the region where the bipolar diffusion contribution<sup>9</sup> to the conductivity by thermally generated electrons and holes in polycrystalline SnSe material.

Figure 4d shows ZT for all SnSe samples. ZT for SnSe hot-pressed at 250°C reaches a maximum of 0.59 at 818 K, which is larger than that ( $ZT_{\max} = 0.5$ ) of polycrystalline SnSe reported by S. Sassi.<sup>4</sup> With increasing hot-pressing temperature, peak ZT increases. For example, peak ZT is 0.60, 0.68, 0.73 and 0.73 for sample hot-pressed at 300°C, 350°C, 400°C and 450°C, respectively. The high ZT for SnSe can be attributed to optimizing the carrier concentration by appropriate control of stoichiometric composition.

## CONCLUSIONS

Nanoparticles SnSe are prepared by using melting and ball-milling technique, and the effect of hot-pressing temperatures on the thermoelectric properties of the dense materials is explored. Due to the optimization of the carrier concentration by appropriate control of stoichiometric composition and the reduction in thermal conductivity, peak ZT value of the compacted material reaches 0.73 for SnSe sample hot-pressed both at 400°C and 450°C, which is 46% larger than that reported by Sassi et al. The present investigation indicates that the thermoelectric performance of the SnSe compound can be significantly improved by sintering with suitable temperature.

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## REFERENCES

1. F.J. Fan, Y.X. Wang, X.J. Liu, L. Wu, and S.H. Yu, *Adv. Mater.* 24, 6158 (2012).

2. L.D. Zhao, S.H. Lo, Y.S. Zhang, H. Sun, G.J. Tan, C. Uher, C. Wolverton, V.P. Dravid, and M.G. Kanatzidis, *Nature* 508, 373 (2014).
3. L.D. Zhao, G.J. Tan, S.Q. Hao, J.Q. He, Y.L. Pei, H. Chi, H. Wang, S.K. Gong, H.B. Xu, V.P. Dravid, C. Uher, G.J. Snyder, C. Wolverton, and M.G. Kanatzidis, *Science* 351, 141 (2016).
4. S. Sassi, C. Candolfi, J.B. Vaney, V. Ohorodniichuk, P. Masschelein, A. Dauscher, and B. Lenoir, *Appl. Phys. Lett.* 104, 212105 (2014).
5. Y.J. Fu, J.T. Xu, G.Q. Liu, J.K. Yang, X.J. Tan, Z. Liu, H.M. Qin, H.Z. Shao, H.C. Jiang, B. Liang, and J. Jiang, *J. Mater. Chem. C* 4, 1201 (2016).
6. H. Wiedemeier and H.G. von Schnering, *Z. Phys. Chem.* 148, 295 (1978).
7. G.J. Snyder and E.S. Toberer, *Nat. Mater.* 7, 105 (2008).
8. D. Li and X.Y. Qin, *J. Appl. Phys.* 100, 023713 (2006).
9. Z. Xiong, X.H. Chen, X.Y. Huang, S.Q. Bai, and L.D. Chen, *Acta Mater.* 58, 3995 (2010).