

# Thermoelectric Properties of Spark Plasma-Sintered $\text{In}_4\text{Se}_3\text{-In}_4\text{Te}_3$

JA YOUNG CHO,<sup>1,2</sup> YOUNG SOO LIM,<sup>1,3</sup> SOON-MOK CHOI,<sup>1</sup>  
KYOUNG HUN KIM,<sup>1</sup> WON-SEON SEO,<sup>1</sup> and HYUNG-HO PARK<sup>2</sup>

1.—Korea Institute of Ceramic Engineering and Technology, 233-5 Gasan-dong, Geumcheon-gu, Seoul 153-801, Korea. 2.—Department of Materials Science and Engineering, Yonsei University, 134 Sinchon-dong, Seodaemun-gu, Seoul 120-749, Korea. 3.—e-mail: yslim@kicet.re.kr

We report the thermoelectric properties of spark plasma-sintered  $\text{In}_4\text{Se}_3\text{-In}_4\text{Te}_3$  materials. For comparison, pure  $\text{In}_4\text{Se}_3$  and  $\text{In}_4\text{Se}_3$  (80 wt.%)/ $\text{In}_4\text{Te}_3$  (20 wt.%) mixture samples were prepared.  $\text{In}_4\text{Se}_3$  and  $\text{In}_4\text{Te}_3$  powders were synthesized by a conventional melting process in evacuated quartz ampoules, and a spark plasma method was used for the sintering of the pure  $\text{In}_4\text{Se}_3$  and mixture samples. Thermoelectric and structural characterizations were carried out, and the mixing effect of  $\text{In}_4\text{Se}_3$  and  $\text{In}_4\text{Te}_3$  on the thermoelectric properties was investigated.

**Key words:**  $\text{In}_4\text{Se}_3$ ,  $\text{In}_4\text{Te}_3$ , mixture, thermoelectric, figure of merit

## INTRODUCTION

$\text{In}_4\text{Se}_3$  consisting of quasi-two-dimensional covalent bond layers and quasi-one-dimensional In chains has received considerable attention because of its superb thermoelectric performance.<sup>1–3</sup> The performance of a thermoelectric material can be quantified by the dimensionless figure of merit,  $ZT = S^2\sigma T/\kappa$ , where  $S$ ,  $\sigma$ ,  $T$ , and  $\kappa$  are the Seebeck coefficient, electrical conductivity, absolute temperature, and thermal conductivity, respectively. The electrical conductivity ( $\sigma$ ) of  $\text{In}_4\text{Se}_3$  with a small direct band gap of 0.2 eV can be controlled by Se-deficient self-doping.<sup>2</sup> A high negative Seebeck coefficient ( $S$ ) of up to  $-500 \mu\text{V/K}$  has been reported, and it is also affected by the self-doping conditions.<sup>2</sup>

Thermal conductivity is a very important factor to obtain high thermoelectric performance.<sup>4,5</sup> It has been reported that very low thermal conductivity ( $\kappa$ ) can be obtained due to the unique features of the low-dimensional structure of  $\text{In}_4\text{Se}_3$ . Peierls distortion by a charge density wave leads to breakage in the translational symmetry, and a condensation state due to strong electron–phonon interactions induces

structural defects in the  $\text{In}_4\text{Se}_3$  lattice.<sup>1,6,7</sup> These defects can restrain the thermal conduction by phonon scattering. Moreover, the abundance of low-frequency phonon modes in  $\text{In}_4\text{Se}_3$  also influences the thermal conductivity.<sup>8,9</sup> Consequently,  $\text{In}_4\text{Se}_3$  can possess a very low thermal conductivity of less than 1.0 W/mK.<sup>1–3</sup>

Interestingly, the space group of  $\text{In}_4\text{Te}_3$  is  $D2h^{12}-P_{mmm}$ , the same as that of  $\text{In}_4\text{Se}_3$ .<sup>10</sup> Therefore, as in  $\text{In}_4\text{Se}_3$ , a low thermal conductivity due to the low-dimensional structure can be expected in  $\text{In}_4\text{Te}_3$ . Moreover, the large mass of the tellurium atoms can impact the thermal conductivity of this class of layered thermoelectric material.<sup>10</sup> Also, the same valences of Se and Te and the similar lattice parameters of  $\text{In}_4\text{Te}_3$  and  $\text{In}_4\text{Se}_3$  may provide the possibility of discovering a new composition in the  $\text{In}_4\text{Se}_3\text{-In}_4\text{Te}_3$  thermoelectric material system.

Herein, we report the thermoelectric properties of the spark plasma-sintered  $\text{In}_4\text{Se}_3\text{-In}_4\text{Te}_3$  material system. Samples of pure  $\text{In}_4\text{Se}_3$  and  $\text{In}_4\text{Se}_3$  (80 wt.%)/ $\text{In}_4\text{Te}_3$  (20 wt.%) mixture were prepared for comparison, and structural, compositional, and thermoelectric characterizations were carried out. The highest  $ZT$  of 0.56 was achieved at 672 K in the mixture sample, and the mixing effect of  $\text{In}_4\text{Se}_3$  and  $\text{In}_4\text{Te}_3$  on the thermoelectric properties was evaluated.

## EXPERIMENTAL PROCEDURES

The In, Se, and Te raw materials were melted in evacuated quartz ampoules by an induction furnace to prepare In-Se and In-Te ingots. For *n*-type self-doping, the nominal compositions of the In-Se and In-Te ingots were controlled to be  $\text{In}_4\text{Se}_{2.5}$  and  $\text{In}_4\text{Te}_{2.8}$ , respectively. Two-step annealing of the In-Se ingot at 535°C for 48 h and 430°C for 24 h was carried out to produce a homogeneous  $\text{In}_4\text{Se}_3$  phase. Thermal annealing for the evolution of the  $\text{In}_4\text{Te}_3$  phase was performed at 420°C for 48 h with the In-Te ingot. The phases were examined by using an x-ray diffractometer (XRD, D/Max-2500/PC, Rigaku).  $\text{In}_4\text{Se}_3$  was synthesized in a single phase, while  $\text{In}_4\text{Te}_3$  contained a small amount ( $\sim 3\%$ ) of an  $\text{In}_2\text{Te}_5$  phase. The annealed  $\text{In}_4\text{Se}_3$  and  $\text{In}_4\text{Te}_3$  ingots were pulverized into powders (8  $\mu\text{m}$  to 30  $\mu\text{m}$ ). Sintered bodies of  $\text{In}_4\text{Se}_3$  and the mixture of  $\text{In}_4\text{Se}_3$  (80 wt.%) and  $\text{In}_4\text{Te}_3$  (20 wt.%) were prepared by spark plasma sintering under a uniaxial pressure of 70 MPa at 390°C for 5 min (SPS-515S, Sumitomo Coal Mining Co.). The densities of the sintered bodies were measured by the Archimedes method, and the results showed that the relative densities of  $\text{In}_4\text{Se}_3$  and the mixture were 100% and 97%, respectively. The compositions of the sintered bodies were characterized by electron probe microanalysis (EPMA, JXA-8100, JEOL). Scanning electron microscopy (SEM) was also performed using the JXA-8100 EPMA. The Seebeck coefficient and electrical conductivity were measured by a four-probe method using a thermoelectric measurement system (RZ-2001i, Ozawa Science). The thermal conductivity was measured by a laser flash method (LFA-457, NETZSCH).

## RESULTS AND DISCUSSION

Figure 1 shows powder XRD patterns of the spark plasma-sintered  $\text{In}_4\text{Se}_3$  and  $\text{In}_4\text{Se}_3$  (80 wt.%)/ $\text{In}_4\text{Te}_3$  (20 wt.%) mixture. The sharp diffraction pattern of the pure  $\text{In}_4\text{Se}_3$  sample indicates that spark plasma sintering is an effective process to produce a sintered body without introducing any secondary phases.<sup>2</sup> However, the intensity of  $\text{In}_4\text{Se}_3$  was drastically weakened in the mixture sample. Therefore, it could be proposed that the existence of an  $\text{In}_4\text{Te}_3$  phase increases the structural instability of the  $\text{In}_4\text{Se}_3$  phase in the mixture sample during the sintering process. Meanwhile, the peaks of  $\text{In}_4\text{Te}_3$  were not observed in the diffraction pattern of the mixture sample, but an  $\text{In}_2\text{Te}_3$  (015) peak was found between the  $\text{In}_4\text{Se}_3$  (330) and (311) peaks, indicating that a phase transformation of  $\text{In}_4\text{Te}_3$  to  $\text{In}_2\text{Te}_3$  occurred during the sintering process.

In this figure, a metallic In phase was also detected in all samples. Although this was not intended, it could be helpful to investigate the exact peak positions of the  $\text{In}_4\text{Se}_3$  phase by using the diffraction peak of In (101) as a reference. Because the sintering process was performed at 390°C under

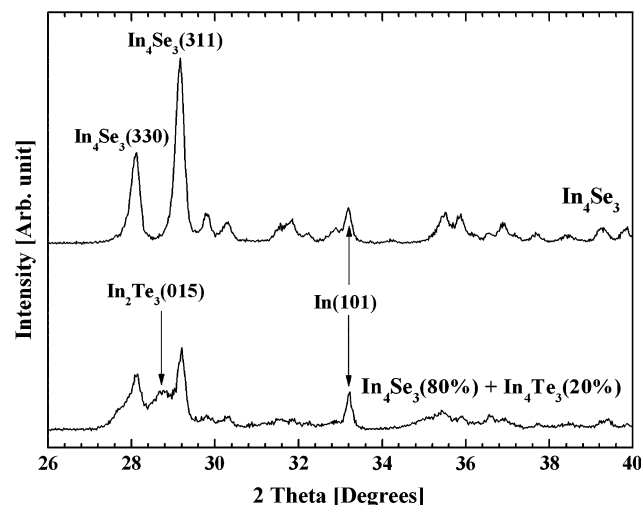


Fig. 1. Powder XRD patterns of spark plasma-sintered  $\text{In}_4\text{Se}_3$  and  $\text{In}_4\text{Se}_3$  (80 wt.%)/ $\text{In}_4\text{Te}_3$  (20 wt.%) mixture samples.

a pressure of 70 MPa, intermixing of Se and Te atoms is quite plausible in the mixture sample. However, there were no significant differences in the peak positions of  $\text{In}_4\text{Se}_3$  in the pure and mixture samples.<sup>2</sup>

Figure 2a shows a SEM micrograph of the pure  $\text{In}_4\text{Se}_3$  sample, and Fig. 2b and c show EPMA mapping images of In and Se, respectively. Numerous small inclusions were observed in Fig. 2a, and the mapping images in Fig. 2b and c confirmed that they precipitated in the sintered body of  $\text{In}_4\text{Se}_3$ . Because the nominal composition of this sample was  $\text{In}_4\text{Se}_{2.5}$  for the self-doping effect, the excess In could be precipitated. Moreover, In precipitation has been reported even in stoichiometric  $\text{In}_4\text{Se}_3$ .<sup>11,12</sup> In the literature, it has been reported that precipitation of In nanoparticles is a result of the decrease in the maximum solubility at the defective region of stoichiometric  $\text{In}_4\text{Se}_3$  and that the concentration of the In nanoparticles decreases while their average size slightly increases during the thermal annealing process.<sup>11</sup> Therefore, the observed In phases in Figs. 1 and 2 could also originate from In nanoparticles merged during the sintering process.

The structure of the  $\text{In}_4\text{Se}_3$  (80 wt.%)/ $\text{In}_4\text{Te}_3$  (20 wt.%) mixture was also investigated by using SEM and EPMA, and the results are shown in Fig. 3. The SEM micrograph in Fig. 3a shows regions in the mixture sample that are distinguishable by their contrast, and the corresponding EPMA mapping images in Fig. 3b–d indicate that the distinctive regions could be categorized by their elemental distributions. Region A, which is composed of only In and Se, could be regarded as the  $\text{In}_4\text{Se}_3$  phase. Because no Te was found in region A, there was no diffusion of Te from  $\text{In}_4\text{Te}_3$  to the  $\text{In}_4\text{Se}_3$  phase during the spark plasma sintering process.

In the B and C regions, all three elements in the mixture sample, In, Te, and Se, were found. The

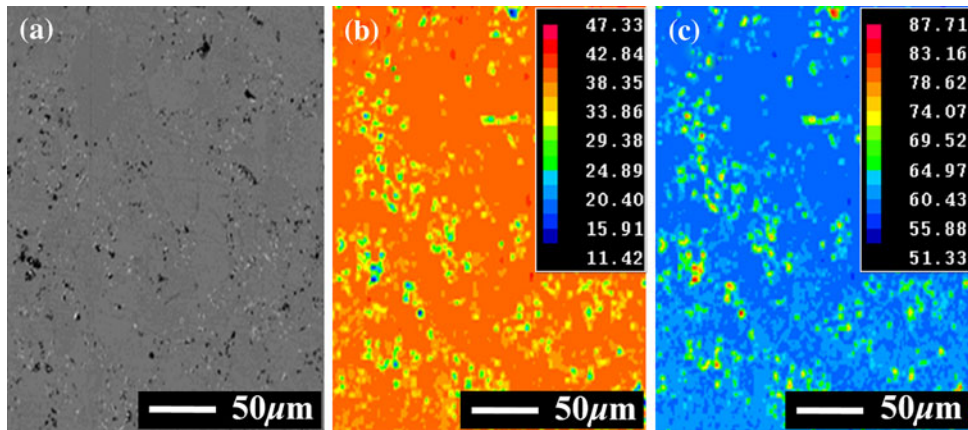


Fig. 2. (a) SEM micrograph of spark plasma-sintered  $\text{In}_4\text{Se}_3$  and corresponding EPMA mapping images of (b) Se and (c) In. The insets indicate the atomic percentages of the elements.

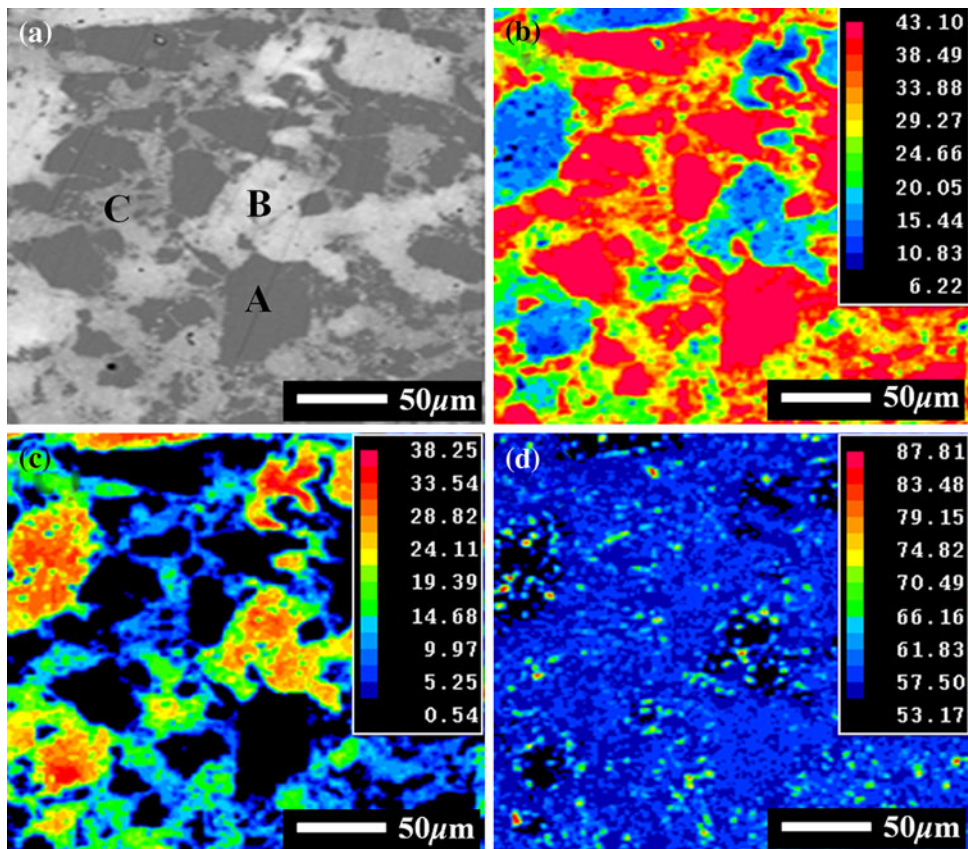


Fig. 3. (a) SEM micrograph of spark plasma-sintered  $\text{In}_4\text{Se}_3$  (80 wt.%) /  $\text{In}_4\text{Te}_3$  (20 wt.%) mixture and corresponding EPMA mapping images of (b) Se, (c) Te, and (d) In. The insets indicate the atomic percentages of the elements.

main differences between the B and C regions were the grain size and the fractions of Se and Te in the In-Se-Te phase. Te was more abundant than Se in the B region, where the grain size was relatively large. In the C region, small grains with high Se and Te concentrations were found. This result shows that the In-Se-Te phase in the B and C regions is formed by diffusion of Se from  $\text{In}_4\text{Se}_3$  to  $\text{In}_4\text{Te}_3$ . Because the atomic number of Te is larger than that

of Se and the lattice constant of  $\text{In}_4\text{Te}_3$  is larger than that of  $\text{In}_4\text{Se}_3$ , preferential diffusion of Se to  $\text{In}_4\text{Te}_3$  is quite reasonable.<sup>10</sup>

Preferential diffusion of Se could lead to deficiency of Se in the  $\text{In}_4\text{Se}_3$  lattices, resulting in a deterioration of crystallinity, as shown in Fig. 1. However, the lattice parameters of  $\text{In}_4\text{Se}_3$  did not change significantly due to the Se deficiency, consistent with the result reported by Rhyee et al.<sup>2</sup> The



$\text{In}_4\text{Te}_3$  phase could also be affected by the preferential diffusion. In Fig. 1, only an  $\text{In}_2\text{Te}_3$  phase was observed and no diffraction peak of the  $\text{In}_4\text{Te}_3$  phase could be observed, in spite of its significant content of 20% in the mixture sample. Therefore, the In-Se-Te phase in the B and C regions is regarded as a  $\text{In}_2(\text{Te}_x\text{Se}_{1-x})_3$  phase, and the Se content in the phase in the C region (small grains) is higher than that in the B region (large grains) due to the more effective diffusion of Se into the small grains. The transformation of the  $\text{In}_4\text{Te}_3$  phase to the  $\text{In}_2\text{Te}_3$  phase was accompanied by In precipitation. As shown in Fig. 3d, precipitated In particles were intensively observed in the B and C regions instead of the A region. Therefore, it is proposed that the  $\text{In}_4\text{Te}_3$  was dissolved into  $2\text{In} + \text{In}_2\text{Te}_3$  during the sintering process and that this process could be accelerated by the preferential diffusion of Se.

Figure 4 shows the electrical conductivities, Seebeck coefficients, and power factors of the pure and mixture samples. As shown in Fig. 4a, the pure  $\text{In}_4\text{Se}_3$  sample had a higher electrical conductivity than the mixture sample at relatively low temperatures. Above 450 K, the conductivities of the pure and mixture samples became nearly identical. From the exponential increase of the electrical conductivity with increasing temperature, it was found that both samples demonstrated semiconducting properties. Below 450 K, the electrical conductivities were higher than the values expected from the exponential increase of the conductivity. Because the temperature of 450 K is slightly higher than the melting temperature of In ( $\sim 430$  K), the transition of the electrical conductivity at this temperature may be related to the melting of the precipitated In.<sup>3</sup> Therefore, the metallic In precipitation shown in Figs. 1 and 2 may be the origin of this transition behavior.

The electrical conductivity is dependent on the carrier concentration and mobility, which are affected by grain size and boundary properties. In this study, the activation energy of the Arrhenius plot in Fig. 1a was  $0.2 \pm 0.02$  eV in both samples at temperatures above 450 K, which is almost the same value as the direct band gap (0.2 eV) of  $\text{In}_4\text{Se}_3$ .<sup>2</sup> Therefore, this implies that thermally excited charge carriers in the  $\text{In}_4\text{Se}_3$  phase may play an important role in the increased electrical conductivity of both samples at high temperatures.

The Seebeck coefficients of the pure and mixture samples were negative, so they were *n*-type thermoelectric semiconductors. The temperature dependence of the absolute Seebeck coefficient is shown in Fig. 4b. The Seebeck coefficient of the pure sample increased with temperature. However, there was no temperature dependence observed for the mixture sample. The Seebeck coefficient of the mixture sample was in the range of  $-250$   $\mu\text{V}/\text{K}$  to  $-290$   $\mu\text{V}/\text{K}$ . In the literature, it was reported that the Seebeck coefficient of  $\text{In}_4\text{Se}_3$  decreases with increasing Se deficiency.<sup>2</sup> In this experiment, the  $\text{In}_4\text{Se}_3$  phase in the mixture sample had a smaller

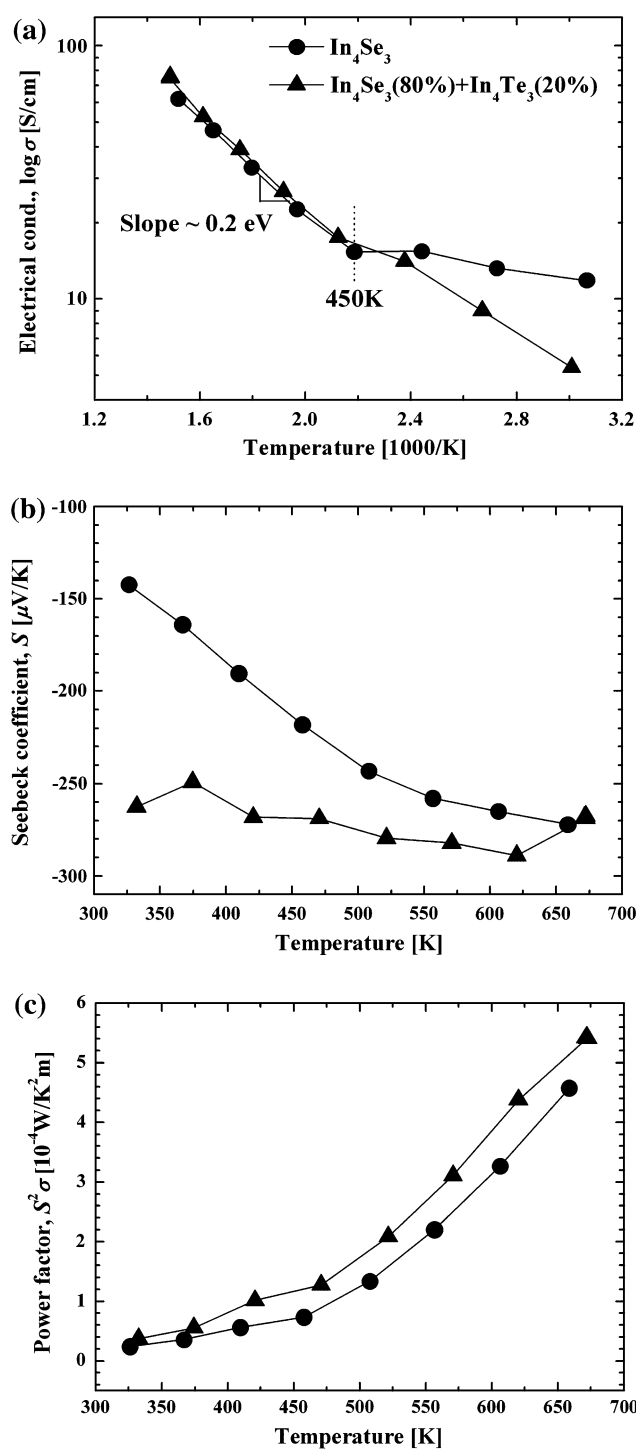


Fig. 4. (a) Arrhenius plot of the electrical conductivity. (b) The Seebeck coefficients and (c) power factors of the pure  $\text{In}_4\text{Se}_3$  and mixture samples.

amount of Se than pure  $\text{In}_4\text{Se}_3$  due to the preferential diffusion of Se, as shown in Fig. 3. Therefore, the increase of the Seebeck coefficient in the mixture may originate from the existence of the  $\text{In}_2\text{Te}_3$  phase. Eventually, the mixture sample shows a higher power factor than the pure  $\text{In}_4\text{Se}_3$  sample, as shown in Fig. 4c.

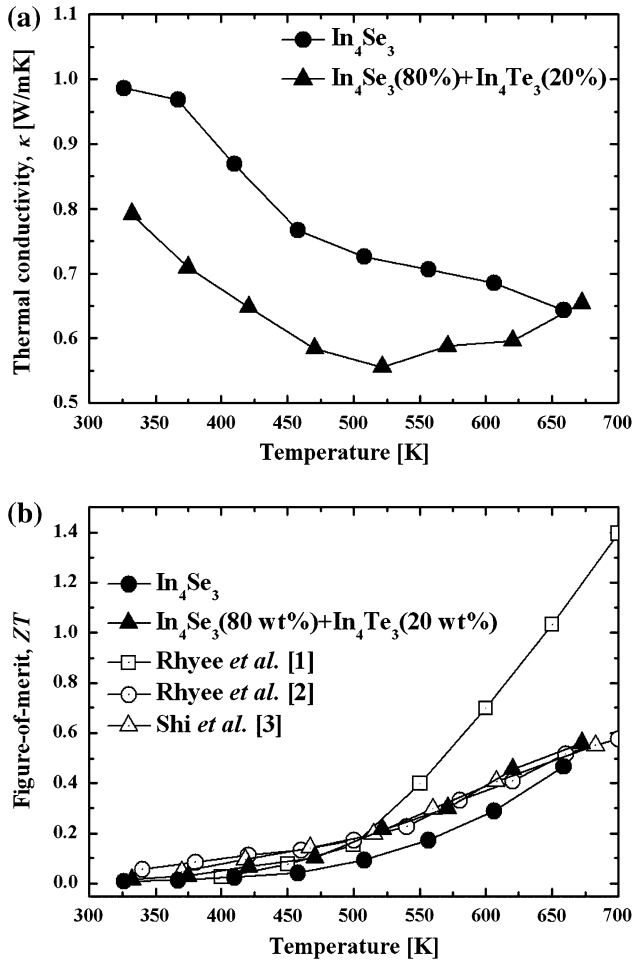


Fig. 5. Temperature dependence of (a) the thermal conductivity and (b) the dimensionless figure of merit of the pure  $\text{In}_4\text{Se}_3$  and mixture samples.

Figure 5 shows the thermal conductivity and dimensionless figure of merit ( $ZT$ ) of the pure and mixture samples. The thermal conductivity of the pure sample monotonically decreased with increasing temperature from 0.97 W/mK to 0.64 W/mK, and is quite similar to that reported in Ref. 2. The origin of such a low thermal conductivity could be Peierls distortion, the condensation state, and the abundance of low-frequency phonon modes in the  $\text{In}_4\text{Se}_3$  structure.<sup>1,6,7,13</sup> In the mixture sample, the thermal conductivity was much lower, and the lowest value of 0.56 W/mK was obtained at 520 K. This indicates that the irregularity of the lattice in the mixture sample could retard the thermal transport even more. Consequently, the highest  $ZT$  of 0.56 at 672 K was obtained in the mixture sample, as shown in Fig. 5b. Although this result is quite similar to the values in Refs. 2 and 3, it was proven that the mixing of  $\text{In}_4\text{Se}_3$  and  $\text{In}_4\text{Te}_3$  is effective to enhance the thermoelectric properties in our material systems. The  $ZT$  of Ref. 1 was obtained from a directionally grown  $\text{In}_4\text{Se}_3$  sample prepared by the Bridgman

method, and its high electrical conductivity is regarded as the main origin of the high  $ZT$ .

As shown above, improved thermoelectric properties were demonstrated in the  $\text{In}_4\text{Se}_3$  (80 wt.%) /  $\text{In}_4\text{Te}_3$  (20 wt.%) mixture sample compared with pure  $\text{In}_4\text{Se}_3$ . In this sample, the increased Seebeck coefficient and lower thermal conductivity could be achieved without a loss of electrical conductivity. This result can provide future possibilities for engineering thermoelectric  $\text{In}_4\text{Se}_3$ -based material systems by alloying or doping.

## CONCLUSIONS

We investigated the structural and thermoelectric properties of spark plasma-sintered  $\text{In}_4\text{Se}_3$  and  $\text{In}_4\text{Se}_3$  (80 wt.%) /  $\text{In}_4\text{Te}_3$  (20 wt.%) mixture samples. In contrast to pure  $\text{In}_4\text{Se}_3$ , a phase transformation from  $\text{In}_4\text{Te}_3$  to  $\text{In}_2\text{Te}_3$  was observed in the mixture sample after the sintering process. Because of the differences in atomic number between Se and Te and in the lattice parameters between  $\text{In}_4\text{Se}_3$  and  $\text{In}_4\text{Te}_3$ , preferential diffusion of Se from  $\text{In}_4\text{Se}_3$  to  $\text{In}_4\text{Te}_3$  was clearly observed in the mixture sample, the effect of which on the structural properties was revealed. The highest  $ZT$  of 0.56 at 672 K was achieved in the mixture sample, and the mixing effect of  $\text{In}_4\text{Se}_3$  and  $\text{In}_4\text{Te}_3$  on the thermoelectric properties was evaluated.

## ACKNOWLEDGEMENTS

This research was supported by a Grant from the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Knowledge Economy, Republic of Korea.

## REFERENCES

1. J.-S. Rhyee, K.H. Lee, S.M. Lee, E. Cho, S.I. Kim, E. Lee, Y.S. Kwon, J.H. Shim, and G. Kotliar, *Nature* 459, 965 (2009).
2. J.-S. Rhyee, E. Cho, K.H. Lee, S.M. Lee, S.I. Kim, H.-S. Kim, Y.S. Kwon, and S.J. Kim, *Appl. Phys. Lett.* 95, 212106 (2009).
3. X. Shi, J.Y. Cho, J.R. Salvador, J. Yang, and H. Wang, *Appl. Phys. Lett.* 96, 162108 (2010).
4. D.T. Morelli, V. Jovovic, and J.P. Heremans, *Phys. Rev. Lett.* 101, 035901 (2008).
5. B. Wölfing, C. Kloc, J. Teubner, and E. Bucher, *Phys. Rev. Lett.* 86, 4350 (2001).
6. D.M. Bercha, L.Y. Kharkhalis, A.I. Bercha, and M. Sznajder, *Phys. Stat. Sol. (b)* 203, 427 (1997).
7. L.S. Kukushkin, *Zh. Eksp. Teor. Fiz. Pis'ma* 7, 194 (1968).
8. D.M. Bercha and K.Z. Rushchanskii, *Phys. Solid State* 40, 1906 (1998).
9. E.G. Lavut, N.V. Chelovskaya, E.V. Anokhina, V.N. Denim, and V.P. Zlomanov, *J. Chem. Thermodyn.* 27, 1337 (1995).
10. D.M. Bercha and K.Z. Rushchanskii, *Phys. Solid State* 41, 1693 (1999).
11. V.M. Garamus, A.K. Islamov, Y.P. Pilat, and V.P. Savchin, *Phys. Solid State* 40, 223 (1998).
12. J.-C. Tedenac, G.P. Vassilev, B. Daouchi, J. Rachidi, and G. Brun, *Cryst. Res. Technol.* 32, 605 (1997).
13. D.M. Bercha, L.Y. Kharkhalis, A.I. Bercha, and M. Sznajder, *Semiconductors* 31, 1118 (1997).