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ARTICLE

Thermoelectric properties and chlorine doping effect of $\text{In}_4\text{Pb}_{0.01}\text{Sn}_{0.03}\text{Se}_{2.9}\text{Cl}_x$ polycrystalline compounds

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We investigated thermoelectric properties of the Cl-doped polycrystalline compounds of $\text{In}_4\text{Pb}_{0.01}\text{Sn}_{0.03}\text{Se}_{2.9}\text{Cl}_x$ ($x = 0.02, 0.04, \text{ and } 0.06$). The x-ray diffraction measurement shows gradual change of lattice volume for $x \leq 0.04$ without any impurity phases indicating systemic change of Cl-doping. The Cl-doping in the compounds has an effect of increasing carrier concentration and effective mass of carriers, resulting in the increase of power factor at high temperature (~ 700 K). Because of the increased electrical conductivity at high temperature, the dimensionless thermoelectric figure-of-merit ZT is reached to 1.25 at 723 K for $x = 0.04$ Cl-doped compound which is relatively high value as n -type polycrystalline materials.

1. Introduction

The global energy crisis makes an issue for not only a development of the new eco-friendly energy sources but also the efficient consumption of the energies currently in use. Thermoelectric research is one of the efforts to promote the energy efficiency. The thermoelectric performance can be defined by the dimensionless figure-of-merit $ZT = S^2\sigma T/\kappa$, where S , σ , κ , and T are Seebeck coefficient, electrical resistivity, thermal conductivity, and absolute temperature, respectively.

The state-of-the-art thermoelectric materials has been reported high ZT values of 2.6 at 923 K (SnSe)¹ and 2.2 at 915 K (SrTe-doped PbTe)². However, the materials with high record of ZT values are mostly focused on p -type materials. We need counterpart n -type materials with high thermoelectric performance in order to make thermoelectric devices.

One of the promising n -type thermoelectric materials is the In_4Se_3 based compounds. The single-crystalline $\text{In}_4\text{Se}_{3-x}$ ($x = 0.65$) was reported high ZT value of 1.48 at 705 K using the Peierls distortion.³ Basically, because the Peierls distortion is based on the quasi-one-dimensional electronic transport, the effect of Peierls distortion is averaged out in polycrystalline materials. Therefore, comparing with single-crystalline materials, the polycrystalline $\text{In}_4\text{Se}_{3-x}$ compounds show decreased ZT values of 0.63 at 710 K and 0.97 at 698 K, synthesized by spark plasma sintering (SPS) and ball milling-hot press sintering methods, respectively.^{4,5}

Recently, the Pb and Sn co-doping on the In_4Se_3 based compounds exhibited largely increased values of thermoelectric performances in spite of polycrystalline compounds. For example, the Pb-/Sn-codoped $\text{In}_4\text{Pb}_x\text{Sn}_y\text{Se}_3$ and the se-deficient

$\text{In}_4\text{Pb}_{0.01}\text{Sn}_{0.03}\text{Se}_{3-x}$ compounds show relatively high ZT value of 1.4 at 733 K and 1.2 ($x=0.1$) at 723 K, respectively.^{6,7}

The other promising route to increase thermoelectric properties on the In_4Se_3 compounds is halogen doping on the compounds $\text{In}_4\text{Se}_{3-x}\text{H}_y$ ($H = \text{F, Cl, Br, and I}$).⁸ The Hall mobilities of the single crystalline $\text{In}_4\text{Se}_{3-x}\text{H}_{0.03}$ are significantly increased by halogen doping. It was found that the Cl-doping is the most effective for increase of Hall mobility. The Cl-doped single crystalline $\text{In}_4\text{Se}_{3-x}\text{Cl}_{0.03}$ ($x = 0.33$) shows high ZT values of maximum ZT 1.53 at 698 K over a wide temperature range as compared with $\text{In}_4\text{Se}_{3-x}$.⁹ The critical issue of the In_4Se_3 based compounds is the increase of chemical potential because the materials are far from the optimum chemical potential from the Boltzmann transport calculation.^{3,9} It has been reported the multiple cation doping and halogen doping on Se-deficient site can increase chemical potential resulting in the enhancement of thermoelectric performance.^{6,10,11}

Here, we investigate the Cl-doping effect on the Pb-/Sn-codoped $\text{In}_4\text{Pb}_{0.01}\text{Sn}_{0.03}\text{Se}_{2.9}\text{Cl}_x$ compounds. In the previous study, we successfully synthesized the polycrystalline $\text{In}_4\text{Pb}_{0.01}\text{Sn}_{0.03}\text{Se}_{2.9}$ compounds without any impurities which showed maximum ZT value of 1.2 at 723 K.⁷ However, the power factor of the $\text{In}_4\text{Pb}_{0.01}\text{Sn}_{0.03}\text{Se}_{2.9}$ compound can increase furthermore because it is still far from the optimized chemical potential 0.8 eV from the Boltzmann transport calculation.^{3,9} The chemical potential of the In_4Se_3 phase can be more increased by electron doping. The Cl-doping is believed to be a good candidate for increase thermoelectric performance in the multiple elements-doped $\text{In}_4\text{Pb}_{0.01}\text{Sn}_{0.03}\text{Se}_{2.9}\text{Cl}_x$ compounds.

2. Experimental

The polycrystalline ingots of $\text{In}_4\text{Pb}_{0.01}\text{Sn}_{0.03}\text{Se}_{2.9}\text{Cl}_x$ ($x=0.02, 0.04,$ and 0.06) were synthesized by melting, quenching, and annealing process. The elements of In, Pb, Sn, and Se, and InCl_2 compound were sealed in evacuated quartz tubes under high vacuum with respect to stoichiometric molar ratios. The quartz ampoules were heated at $1,123\text{K}$ for 24 h with following water quenching.

The ingots were pulverized and sintered under argon atmosphere by hot-press at about 730K for 1 h under uniaxial pressure of 70MPa . In order to increase thermal stability, the pellets were annealed at 753K for 5 days. The relative densities of annealed samples are above 95 % ($5.82 \sim 5.93\text{g/cm}^3$) of the theoretical density.

The crystal structure and phase of annealed samples are identified by the powder x-ray diffraction (XRD) using $\text{Cu } \alpha$ radiation (D8 advance, Bruker). The Rietveld refinement was carried out using FullProf software. The electrical resistivity ρ and Seebeck coefficient S were measured under an argon atmosphere by four-probe method using a thermoelectric properties measure system (ZEM-3, ULVAC-RIKO, Japan). The carrier concentration was calculated by the relation of $n_H = -1/(R_H e)$ where R_H is Hall coefficient. The Hall coefficient R_H ($R_H = \rho_{xy}/H$) and Hall resistivity ρ_{xy} were measured by four-probe contact method with sweeping magnetic fields from -5T to 5T using physical property measurement system (PPMS, Quantum Design, USA). We obtained the thermal conductivity from the relation of $\kappa = \lambda \rho_s C_p$, where λ , ρ_s , and C_p are thermal diffusivity, sample density, and specific heat, respectively. The thermal diffusivity λ and specific heat C_p were measured by laser flash method (LFA-457, NETZSCH) and physical property measurement system, respectively.

3. Results and Discussion

Figure 1 shows Rietveld refinement analysis on powder X-ray diffraction (XRD) patterns of the prepared samples ($x = 0.02$ and $x = 0.04$) based on the orthorhombic $Pnmm$ space group, respectively. The XRD patterns show a single phase of In_4Se_3 with no noticeable impurity peaks except $x = 0.06$. Because of impurity phase of InSe (Hexagonal, No. 194), we cannot analyse the XRD pattern by Rietveld refinement for the $x = 0.06$ compound. It indicates that the $x = 0.06$ is in the solubility limit of chlorine which induces the phase separation from In_4Se_3 to InSe phase. The lattice parameter is calculated as shown in Table 1. In the previous investigation of Se-deficient Pb/Sn co-doped compounds $\text{In}_4\text{Pb}_{0.01}\text{Sn}_{0.03}\text{Se}_{3-x}$ ($x=0.1, 0.2, 0.3, 0.4,$ and 0.5), the lattice parameters are systemically changed.⁷ However, the lattice parameters of Cl-doped samples $\text{In}_4\text{Pb}_{0.01}\text{Sn}_{0.03}\text{Se}_{2.9}\text{Cl}_x$ do not show the systematic changes but show a decrease of lattice volume (inset of Fig. 1) with increasing chlorine concentration up to $x = 0.04$ compound. Because the compound of $x = 0.06$ has InSe impurity phase, the lattice volume of the compound does not show systematic change.

From the formation energy calculation of halogen-substituted $\text{In}_4\text{Se}_{3-x}\text{H}_{0.03}$ compound, the substitution and vacancy occupation at Se3-site by Cl-doping is the most stable state in $\text{In}_4\text{Se}_{3-x}$.⁸ The decrease of lattice volume by Cl-doping can be understood by the

strong Coulomb interaction from the electronegativity of Cl and the Cl-substitution at Se3 site.¹²

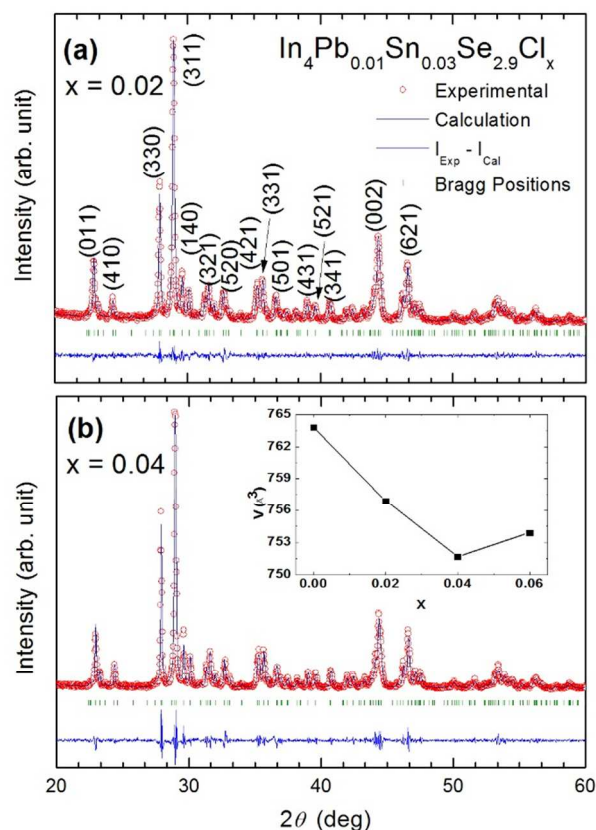


Fig. 1 Powder x-ray diffraction profiles of $\text{In}_4\text{Pb}_{0.01}\text{Sn}_{0.03}\text{Se}_{2.9}\text{Cl}_x$ compounds (a) $x = 0.02$ and (b) $x = 0.04$. Reliability factors (R-factor) obtained from the fitting are as follows. $x = 0.02$: $R_p = 6.75$, $R_{wp} = 8.78$, $R_{exp} = 7.30$; $x = 0.04$: $R_p = 9.10$, $R_{wp} = 11.3$, $R_{exp} = 7.34$. Inset of (b) shows the lattice volume with respect to Cl concentration of the compounds.

x	a (Å)	b (Å)	c (Å)	V (Å ³)
0.00*	15.29	12.24	4.08	764
0.02	15.19	12.29	4.06	757
0.04	15.20	12.19	4.06	752
0.06	15.22	12.20	4.06	754

Table 1 The lattice parameters of $\text{In}_4\text{Pb}_{0.01}\text{Sn}_{0.03}\text{Se}_{2.9}\text{Cl}_x$ ($x = 0.0, 0.02, 0.04,$ and 0.06). (*Ref. 7)

The temperature dependent electrical resistivity of the polycrystalline $\text{In}_4\text{Pb}_{0.01}\text{Sn}_{0.03}\text{Se}_{2.9}\text{Cl}_x$ ($x = 0.02, 0.04,$ and 0.06) compounds and $x = 0.0$ (Ref. 7) are presented in Fig. 2(a). The electrical resistivity of Cl-doped compounds shows the semiconducting behaviour in the measured temperature range. The increasing electrical resistivity with increasing Cl doping shows a similar behaviour as $\text{In}_4\text{Se}_{2.7}\text{Cl}_x$.¹⁰

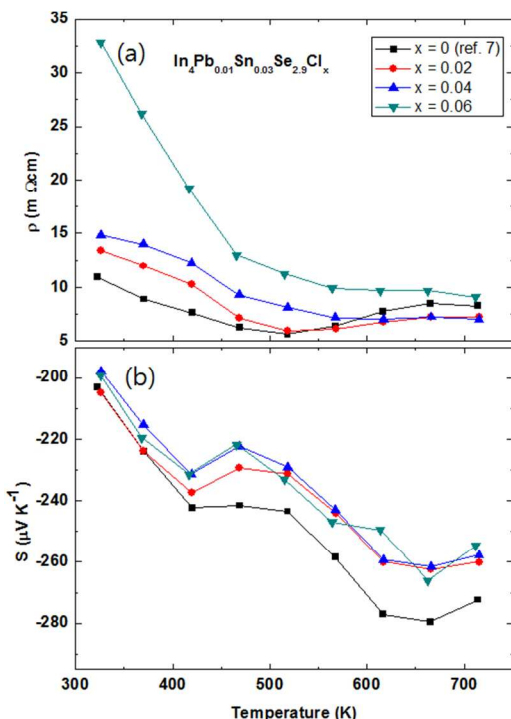


Fig. 2 Temperature-dependent electrical resistivity $\rho(T)$ (a) and Seebeck coefficient $S(T)$ (b) of the $\text{In}_4\text{Pb}_{0.01}\text{Sn}_{0.03}\text{Se}_{2.9}\text{Cl}_x$ ($x = 0.0, 0.02, 0.04, \text{ and } 0.06$) compounds.

The electrical resistivity has a relation with $\rho = ne\mu$, where n , e , and μ are Hall carrier concentration, electric charge, and Hall mobility of carrier. From the Hall resistivity ρ_{xy} and electrical resistivity ρ measurements, we obtain the effective carrier concentration n_H and Hall mobility μ_H , which are listed in Table 2. The carrier concentration of the $\text{In}_4\text{Pb}_{0.01}\text{Sn}_{0.03}\text{Se}_{2.9}\text{Cl}_x$ ($x = 0.02$) compound shows the value of 1.58 times higher than the one of pristine $\text{In}_4\text{Pb}_{0.01}\text{Sn}_{0.03}\text{Se}_{2.9}$ compound. The carrier concentration is not increased with Cl doping for $x = 0.04$ and 0.06 , implying the solubility limit of the compounds as in the case of the polycrystalline $\text{In}_4\text{Se}_{2.7}\text{Cl}_x$ compounds ($x = 0 \sim 0.05$).¹⁰

x	n_H ($\times 10^{18}$ cm^{-3})	ρ ($\text{m}\Omega\text{-cm}$)	μ_H ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	$-S$ ($\mu\text{V}/\text{K}$)	m^* (m_e)
0.00	2.67	10.9	214	203	0.18
0.02	4.22	13.4	111	205	0.25
0.04	4.09	14.9	103	198	0.24
0.06	3.99	32.9	48	199	0.23

Table 2 The Hall carrier concentration n_H , electrical resistivity ρ , Hall mobility μ_H , negative Seebeck coefficient $-|S|$, and effective mass of carrier m^* of the $\text{In}_4\text{Pb}_{0.01}\text{Sn}_{0.03}\text{Se}_{2.9}\text{Cl}_x$ ($x = 0, 0.02, 0.04, \text{ and } 0.06$) compounds at 320 K.

The Hall mobilities of the $\text{In}_4\text{Pb}_{0.01}\text{Sn}_{0.03}\text{Se}_{2.9}\text{Cl}_x$ compounds are decreased with increasing Cl-doping. In contrast with the result of $\text{In}_4\text{Se}_{3-x}\text{Cl}_{0.03}$ single crystal,⁹ the polycrystalline compounds of $\text{In}_4\text{Se}_{2.7}\text{Cl}_x$ ¹⁰ and $\text{In}_4\text{Pb}_{0.01}\text{Sn}_{0.03}\text{Se}_{2.9}\text{Cl}_x$ decreased the Hall mobility by increasing the Cl-doping. It implies that the Hall mobility of

polycrystalline In_4Se_3 is decreased by the excess Cl-impurity scattering at the grain boundary. However, the CuBr-doped $\text{In}_4\text{Se}_{2.5}$ poly crystal shows the increased Hall mobility.¹³

The increase of Hall mobility in bulk crystalline materials is caused by the enhancement of crystallinity in chlorine doped In_4Se_3 .⁹ For example, the x-ray diffraction patterns for the cross-sectional planes of crystalline ingots show well aligned crystal orientation. However, for polycrystalline materials, the Hall mobility of chlorine doped samples is decreased with increasing chlorine doping concentration.¹⁰ It implies that the chlorine itself acts as scattering centre of carriers but it helps to enhance crystallinity during crystal growth. The doped chlorine can increase Hall carrier density, but an excess chlorine can precipitate at the grain boundaries, resulting in the decrease of Hall mobility. On the other hand, the single crystalline materials have less effect on grain boundary, thereby the enhanced crystallinity can increase Hall mobility of carriers.

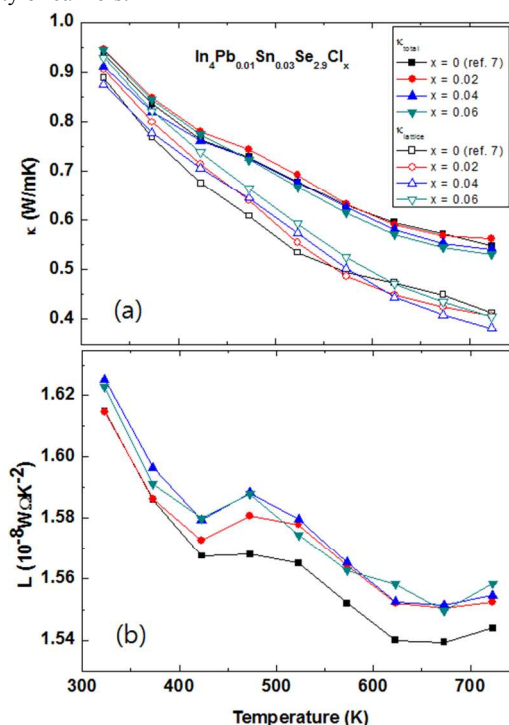


Fig. 3 Temperature-dependent total thermal conductivity κ_{tot} (closed symbols), lattice thermal conductivity κ_{ph} (a), and Lorenz number $L(T)$ (b) of the $\text{In}_4\text{Pb}_{0.01}\text{Sn}_{0.03}\text{Se}_{2.9}\text{Cl}_x$ ($x = 0.0, 0.02, 0.04, \text{ and } 0.06$) compounds.

The temperature dependent Seebeck coefficient $S(T)$ of the polycrystalline $\text{In}_4\text{Pb}_{0.01}\text{Sn}_{0.03}\text{Se}_{2.9}\text{Cl}_x$ ($x = 0.02, 0.04, \text{ and } 0.06$) compounds are decreased with Cl-doping as compared with $x = 0.0$ as shown Fig. 2(b). The Seebeck coefficient of degenerate semiconductors can be expressed as in the following equation.

$$S = \frac{8\pi^2 \kappa_B^2}{3e\hbar^2} m^* T \left(\frac{\pi}{3n} \right)^{2/3}$$

where m^* and n are the effective mass of carrier and carrier concentration, respectively.¹⁴ From the Hall carrier concentration and the measured Seebeck coefficient, the calculated effective mass

of carrier are listed in Table 2. The effective mass of carrier of $x = 0.02$ sample is obviously increased as compared the one of $x = 0.0$, even though the Cl-doping dependence is not clear. The increased effective mass of carrier indicates less dispersive electron band than the non-Cl-doped sample. From the effective thermal band gap relation, $E_g = 2eS_{max}T_{max}$,¹⁵ we can estimate the band gap as 0.372 eV ($x = 0.0$)⁷ and 0.347 eV ($x = 0.04$). The Cl-doping on the $\text{In}_4\text{Pb}_{0.01}\text{Sn}_{0.03}\text{Se}_{2.9}\text{Cl}_x$ compounds induces the less dispersive and decreased band gap than those of the $\text{In}_4\text{Pb}_{0.01}\text{Sn}_{0.03}\text{Se}_{2.9}$ compound.

The total thermal conductivities of the polycrystalline $\text{In}_4\text{Pb}_{0.01}\text{Sn}_{0.03}\text{Se}_{2.9}\text{Cl}_x$ ($x = 0, 0.02, 0.04$ and 0.06) compounds are presented in Fig. 3(a). The thermal conductivities of ($x = 0.0, 0.02, 0.04$, and 0.06) are decreased with increasing temperature. This conventional $1/T$ behaviour is mainly caused by an acoustic phonon contribution for the thermal transport. There is no systematic change of the $\kappa(T)$ with respect to Cl-doping concentration.

In general, the total thermal conductivity κ is composed of electrical κ_{el} and lattice thermal conductivity κ_{ph} . The electronic thermal conductivity κ_{el} can be calculated by the Wiedemann-Franz law $\kappa_{el} = L_0\sigma T$, where L_0 , σ , and T are the Lorenz number, electrical conductivity, and absolute temperature, respectively. In usual cases, the Lorenz number is written as:

$$L_0 = \frac{\pi^2}{3} \left(\frac{k_B}{e} \right)^2 = 2.45 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$$

However, the Lorenz number is incorrect in correlated metal and many degenerated semiconductors. In order to get a more reliable Lorenz number, we calculated the Lorenz number by using the following equation:⁷

$$L = \left(\frac{k_B}{e} \right)^2 \left(\frac{(r + \frac{7}{2})F_{r+\frac{5}{2}}(\eta)}{(r + \frac{3}{2})F_{r+\frac{1}{2}}(\eta)} - \left[\frac{(r + \frac{5}{2})F_{r+\frac{3}{2}}(\eta)}{(r + \frac{3}{2})F_{r+\frac{1}{2}}(\eta)} \right]^2 \right)$$

where r is the scattering parameter, $\eta = E_F/k_B T$ is the reduced Fermi energy, and $F_n(\eta)$ is the n -th order Fermi integral given by

$$F_n(\eta) = \int_0^\infty \frac{x^n}{1 + e^{x-\eta}} dx$$

For most cases, the scattering parameter for acoustic phonon scattering is $r = -1/2$. When we fit the measured Seebeck coefficient to the following equation with a free parameter η , we can get the Fermi integral η :

$$S = \pm \frac{k_B}{e} \left\{ \frac{(r + \frac{5}{2})F_{r+\frac{3}{2}}(\eta)}{(r + \frac{3}{2})F_{r+\frac{1}{2}}(\eta)} - \eta \right\}$$

By using the Fermi integral, the calculated temperature dependent Lorenz numbers of $\text{In}_4\text{Pb}_{0.01}\text{Sn}_{0.03}\text{Se}_{2.9}\text{Cl}_x$ ($x = 0.0, 0.02, 0.04$, and 0.06) are shown in Fig. 3(b). The calculated temperature dependent Lorenz number is lower than the conventional Lorenz number $L_0 = 2.45 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$. The low Lorenz numbers indicate that the electrical contribution for thermal transport is lower than conventional metals. Using the calculated Lorenz number and electrical resistivity, we can obtain the lattice thermal conductivity by subtracting the electrical thermal conductivity from the total thermal conductivity as shown Fig. 3(a) (open symbols). The change of lattice thermal conductivity with respect to chlorine doping

concentration of $\text{In}_4\text{Pb}_{0.01}\text{Sn}_{0.03}\text{Se}_{2.9}\text{Cl}_x$ ($x = 0.0, 0.02, 0.04$, and 0.06) is not obvious. The similar thermal conductivity can be explained by the similarity of crystal structure and phonon dispersion relation between In_4Se_3 and InSe .¹⁶

Fig. 4(a) shows the temperature dependent power factor $S^2\sigma$ of the polycrystalline $\text{In}_4\text{Pb}_{0.01}\text{Sn}_{0.03}\text{Se}_{2.9}\text{Cl}_x$ ($x = 0.0, 0.02, 0.04$, and 0.06) compounds. The decreased power factor with increasing Cl-doping is mainly caused by the decreased Hall mobility near room- and mid-temperature range. On the other hand, the slightly increased power factors of $x = 0.02$ and 0.04 are obtained near 723 K. The compound of $x = 0.06$ shows a decreased power factor than the other samples ($x = 0.0, 0.02$, and 0.04) implying that the InSe phase separation is not good for increasing power factor in the In_4Se_3 phase.

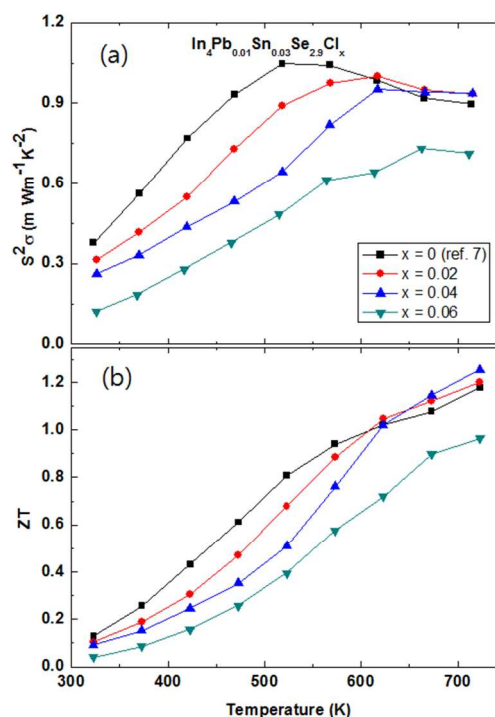


Fig. 4 Temperature-dependent power factor $S^2\sigma$ (a) and ZT values (b) of the $\text{In}_4\text{Pb}_{0.01}\text{Sn}_{0.03}\text{Se}_{2.9}\text{Cl}_x$ ($x = 0.0, 0.02, 0.04$ and 0.06) compounds.

The ZT values of the polycrystalline $\text{In}_4\text{Pb}_{0.01}\text{Sn}_{0.03}\text{Se}_{2.9}\text{Cl}_x$ ($x = 0.0, 0.02, 0.04$, and 0.06) compounds are presented in Fig. 4(b). The maximum ZT of $x = 0.04$ reaches up to 1.25 at 723 K, which is slightly increased value as compared with the one of pristine compound $x = 0.0$ ($ZT = 1.2$). The high ZT value over a wide temperature range in bulk crystals $\text{In}_4\text{Se}_{3-x}\text{Cl}_{0.03}$ (1.53) is caused by the significant increase of Hall mobility which is attributed from the enhancement of crystallinity by chlorine doping.⁹ Because the polycrystalline $\text{In}_4\text{Se}_{2.7}\text{Cl}_x$ samples exhibit decreased ZT (0.67) value with increasing chlorine doping concentration, we believe that further enhancement of ZT can be possible in the compounds of $\text{In}_4\text{Pb}_{0.01}\text{Sn}_{0.03}\text{Se}_{2.9}\text{Cl}_x$ for single crystalline form. Therefore we should investigate the thermoelectric properties of the single crystalline compounds as a further research.

Conclusions

The Cl-doped polycrystalline $\text{In}_4\text{Pb}_{0.01}\text{Sn}_{0.03}\text{Se}_{2.9}\text{Cl}_x$ ($x = 0.0, 0.02, 0.04, \text{ and } 0.06$) compounds are synthesized well by the melting and solid state reaction with systemic change of lattice volume. Because of the chlorine impurity scattering, the electrical resistivities of the Cl-doped samples ($x = 0.02, 0.04, 0.06$) are increased as compared with non-Cl-doped sample ($x = 0.0$) near room temperature which is mainly caused by the decrease of Hall mobility by chlorine doping. However, the electrical resistivities of $x = 0.02$ and 0.04 are decreased at high temperature accompanying with smearing out of broad shoulder near 670 K.

Consequently, it exhibits relatively low thermal conductivity and high power factor over a wide temperature range. The power factor and ZT values of the Cl-doped compounds ($x = 0.02$ and 0.04) were increased as compared with the non Cl-doped compound ($x = 0.0$) near 700 K. The maximum ZT value of 1.25 is relatively high ZT for polycrystalline In_4Se_3 based compounds. Further enhancement of thermoelectric performance can be expected in single crystalline compounds by promoting crystallinity of the samples.

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Notes and references

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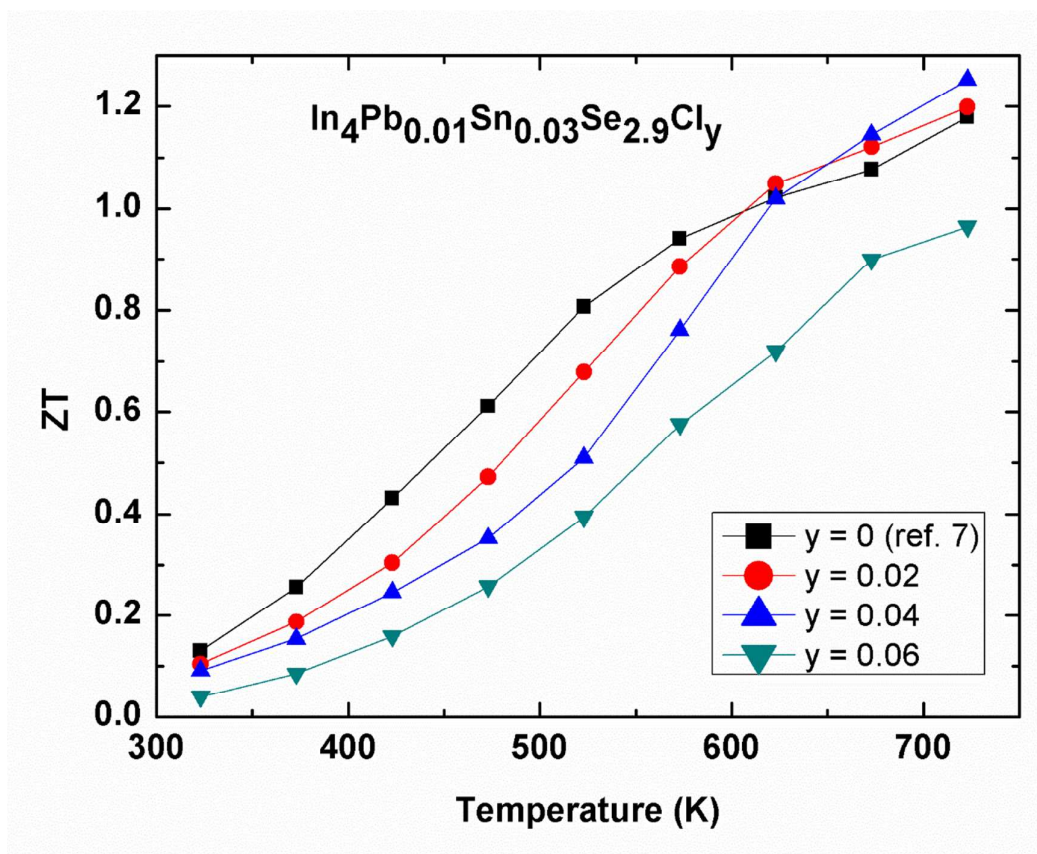
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- 1 L.-D. Zhao, S.-H. Lo, Y. Zhang, H. Sun, G. Tan, C. Uher, C. Wolverton, V. P. Dravid, M. G. Kanatzidis, *Nature (London)*, 2014, **508**, 373.
- 2 K. Biswas, J. He, I. D. Blum, C.-I. Wu, T. P. Hogan, D. N. Seidman, V. P. Dravid, M. G. Kanatzidis, *Nature (London)*, 2012, **489**, 414.
- 3 J.-S. Rhyee, K. H. Lee, S. M. Lee, E. Cho, S. I. Kim, E. Lee, Y. S. Kwon, J. H. Shim, G. Kotliar, *Nature (London)*, 2009, **459**, 965.
- 4 J.-S. Rhyee, E. Cho, K. H. Lee, S. M. Lee, S. I. Kim, H. -S. Kim, Y. S. Kwon, S. J. Kim, *Appl. Phys. Lett.*, 2009, **95**, 212106.
- 5 G. H. Zhu, Y. C. Lan, H. Wang, G. Joshi, Q. Chen, Z. F. Ren *Phys. Rev. B*, 2011, **83**, 115201.

- 6 Z.-S. Lin, L. Chen, L. -M. Wang, J. -T. Zhao, L.-M. Wu, *Adv. Mater.*, 2013, **25**, 4800.
- 7 J. H. Kim, M. J. Kim, S. Oh, J.-S. Rhyee, *J. Alloys. Comp.*, 2014, **615**, 933.
- 8 K. Ahn, E. Cho, J.-S. Rhyee, S. I. Kim, S. Hwang, H. -S. Kim, S. M. Lee, K. H. Lee, *J. Mater. Chem.*, 2012, **22**, 5730.
- 9 J.-S. Rhyee, K. Ahn, K. H. Lee, H. S. Ji, J.-H. Shim, *Adv. Mater.*, 2011, **23**, 2191.
- 10 J.-S. Rhyee, D. Choi, *J. Appl. Phys.*, 2011, **110**, 083706.
- 11 K. Ahn, E. Cho, J. -S. Rhyee, S. I. Kim, S. M. Lee, K. H. Lee, *Appl. Phys. Lett.*, 2011, **99**, 102110.
- 12 R. T. Sanderson, *J. Am. Chem. Soc.*, 1983, **105**, 2259.
- 13 Y. Luo, J. Yang, G. Liu, Y. Xiao, L. Fu, W. Li, P. Zhu, J. Peng, S. Gao, J. Zhang, *Adv. Energy Mater.* 2014, **4**, 1300599
- 14 A. F. Ioffe, *Semiconductor Thermoelements and Thermoelectric Cooling*, Infosearch, 1957.
- 15 H. J. Goldsmid, J. W. Sharp, *J. Electron. Mater.*, 1999, **28**, 869.
- 16 M. Sznajder, K. Z. Rushchanskii, L. Yu. Kharkhalis, D. M. Bercha, *Phys. Stat. Sol.*, 2006, **243**, 2006

Table of Content Entry Figure



Enhanced thermoelectric figure-of-merit $ZT = 1.25$ at 723 K for n-type $\text{In}_4\text{Pb}_{0.01}\text{Sn}_{0.03}\text{Se}_{2.9}\text{Cl}_x$ ($x = 0.04$) polycrystalline materials.