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# Thermoelectric properties of solid solutions based on tin telluride

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**Abstract**. The relation of a thermoelectric parameters of the solid solutions based on tin telluride: SnTe-MnTe, SnTe-$Cu_2Te$ and SnTe-$In_2Te_3$: Pb versus an amount of dopant impurity are investigated. The crystaloquasichemical mechanism of the solid solutions formation are proposed. Showed is that at the expense of essential decreasing of a thermal conductivity factor in the solid solutions the improvement of the basic thermoelectric parameters of the material takes place. The compositions which have a maximum values of the thermoelectric Q-factor are retrieved.

**Keywords:** tin telluride, solid solutions, thermoelectric parameters, crystaloquasichemical mechanism.

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## 1. Introduction

Telluride of tin — one of a perspective materials for the positive branch of thermoelements. It becames to the nonstoichiometric compounds and crystallizes in the structure like NaCl with an excess of tellurium (50,4 at. % Te at 790 K) with the opened maximum. The latter is the cause of formation of the cation vacancies and very high hole concentrations ($10^{20}$–$10^{21}$ $cm^{-3}$) in a valence band. Width of the band gap of SnTe at 300 K makes 0.26 eV [1].

It is known [2], that the thermoelectric *Q*-factor (*Z*) of material is determined as

$$Z = \alpha^2 \sigma \chi^{-1}, \tag{1}$$

where $\alpha$ – thermoelectric *Q*-factor, $\sigma$ – electrical conductivity and $\chi$ – thermal conductivity respectively. All quantities which are included in the expression (1) are functions of temperature and carrier concentrations. In this connection operational use of semiconductors in a thermoelectricity is always bounds with necessity of doping of material. It is point, that as though not to optimizate the thermoelectric parameters by the values of concentration of carriers or temperature, at high thermal conductivity the thermoelectric *Q*-factor always will be small. Therefore, further investigations are connected with searching of materials that have low thermal conductivity. It is possible to be done at the expense of the isovalent substitution [2].

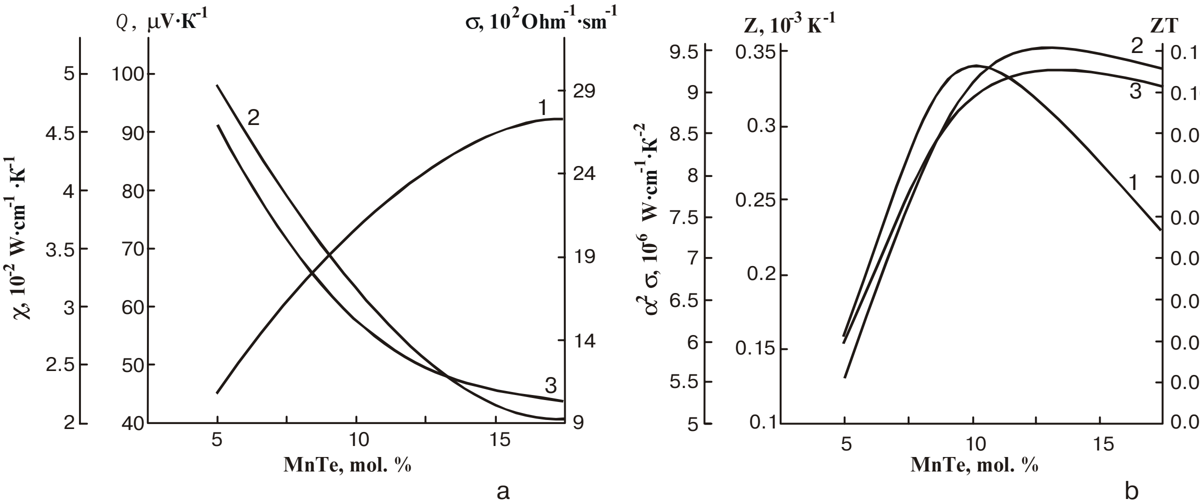
In this work, investigated is the influence of the cation substitution in tin telluride on change of the basic thermoelectric parameters of the solid solutions based on SnTe. The problem of the optimization of the thermoelectric *Q*-factor is discussed.

## 2. The experimental technique and results of investigations

Solid solutions SnTe-MnTe (A), SnTe-$Cu_2Te$ (B), and also SnTe-$In_2Te_3$:Pb (C) were investigated. The alloys synthesized from separate components of a high scale of purity (nominally 99.999 % pure of basic component) in vacuum ($10^{-1}$–$10^{-3}$ Pa) quartz ampulas at 1270-1420 K. After air cooling the samples yielded homogeneous sintering at 870-970 K during 300-310 hours accordingly with following (cooling) hardening in ice water. On the obtained samples, measurements of the thermoelectric parameters at the room temperature are fulfilled accordingly to techniques [3].

The results of the measured relations of the thermoelectric parameters of solid solutions versus composition are shown in Figs 1-3. For the crystals such as A in the range of ~15 mol.% MnTe the bend of concentration dependences (Fig. 1) takes place, which is connected with saturation up to the solubility limit of the solid solution [4]. Thus, increasing of the thermoelectric *Q*-factor (Fig. 1a, curve 1) and decreasing of the thermal conductivity (Fig. 1a, curve 3) at decreasing electrical conductivity (Fig. 1a, curve 2) leads to the considerable general improvement of the thermoelectric parameters (Fig. 1b) with increasing content of MnTe within a range of homogeneity..

Thermoelectric parameters of the crystals such as B also essentially depend on content of copper telluride in the solid solution [5]: its increase to 3 mol. % leads to increase of the thermoelectric *Q*-factor (Fig. 2a, curve 1), decreasing of the electrical conductivity (Fig. 2b, curve 2) and thermal conductivity (Fig. 2a, curve 3). In this concentration range, the considerable improvement of the thermoelectric parameters of this material (Fig. 2b) takes place. At further increase of copper telluride amount in the solid solution $(SnTe)_{1-x}(Cu_2Te)_x$ ($x > 0,03$) even at increasing of the electrical conductivity (Fig. 2a, curve 2) and decreasing of a value of the thermal conductivity factor (Fig. 1a, curve 3), the diverse thermoelectric parameters have the legible tendency to decreasing (Fig. 2a, curve 1, Fig. 2b).



a b

**Fig. 1.** Composition dependence of the thermoelectric properties of the SnTe-MnTe alloy at 300 K:
a – thermoelectric Q-factor ($\alpha$ – 1), electroconductivity ($\sigma$ – 2), lattice thermal conductivity ($\chi$ – 3);
b – thermoelectric power ($\alpha^2\sigma$ – 1), thermoelectric quality (Z – 2), dimensionless thermoelectric quality (ZT -3).

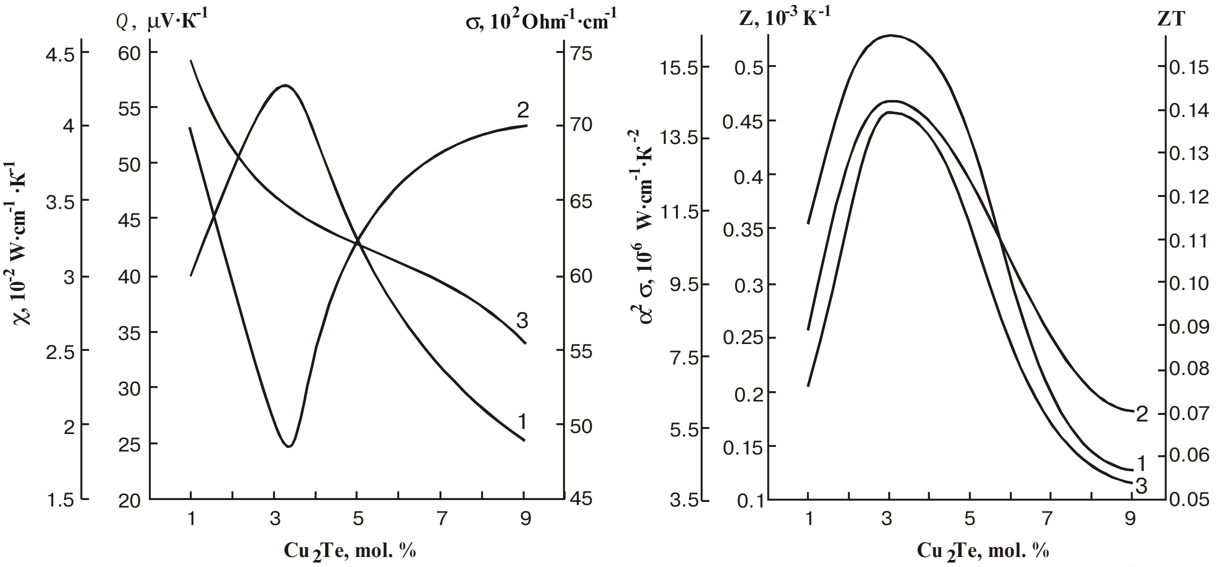


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**Fig. 2.** Composition dependence of the thermoelectric properties of the SnTe-$Cu_2Te$ alloy at 300 K:
a – thermoelectric Q-factor ($\alpha$ – 1), electroconductivity ($\sigma$ – 2), lattice thermal conductivity ($\chi$ – 3);
b – thermoelectric power ($\alpha^2\sigma$ – 1), thermoelectric quality (Z – 2), dimensionless thermoelectric quality (ZT – 3).

Increase of lead amount in previously doped tin telluride up to 2 mol.% $In_2Te_3$ leads to increasing the thermoelectric *Q*-factor (Fig. 3a, curve 1), decreasing of the electrical conductivity (Fig. 3a, curve 2) and thermal conductivity factor (Fig. 3a, curve 3) [6]. At a general tendency of decreasing the thermoelectric power (Fig. 3, curve 1), values of the thermoelectric *Q*-factor and the dimensionless values ZT are characterized by a legible maximum in the range of 0.4 at.% Pb (Fig. 3, curves 2, 3).

## 3. Discussion of results

The general property for the investigated solid solutions based on tin telluride is decreasing of the thermal conductivity factor in borders of a homogeneity range (Figs 1-3a, curves 3). This can be associated with increasing of defectness degree of the crystal structure, which leads to increasing phonon dissipation and decreasing the thermal conductivity factor.

The processes which take place at cation substitution in tin telluride (formula – SnTe, antistructure – $V''_{Sn}V^{\cdot\cdot}_{Te}$, where $V_{Sn}$, $V_{Te}$ – vacancies of tin and tellurium, and «-», «+» are negative and positive charges, respectively) can be described by the crystaloquasichemical equations [7].

### *3.1. Solid solutions SnTe – MnTe (A)*

The superposition of the crystalochemical composition of a dopant compound $Mn_2Te_2$ on the antistructure of the basic matrix leads to formation of the cluster, that at a superposition with the quasichemical formula of the stoichiometric composition of tin telluride will be described by the crystaloquasichemical transformations:

$$\begin{aligned}&V''_{\mathrm{Sn}}V^{\cdot\cdot}_{\mathrm{Te}}+\mathrm{Mn}^{2+}\mathrm{Te}^{2-}\rightarrow\mathrm{Mn}^{\times}_{\mathrm{Sn}}\mathrm{Te}^{\times}_{\mathrm{Te}}\\&(1-\alpha)\mathrm{Sn}^{\times}_{\mathrm{Sn}}\mathrm{Te}^{\times}_{\mathrm{Te}}+\alpha(\mathrm{Mn}^{\times}_{\mathrm{Sn}}\mathrm{Te}^{\times}_{\mathrm{Te}})\rightarrow\\&\rightarrow(\mathrm{Sn}^{\times}_{1-\alpha}\mathrm{Mn}^{\times}_{\alpha})_{\mathrm{Sn}}\mathrm{Te}^{\times}_{\mathrm{Te}}\end{aligned}\tag{2}$$

It is obvious, that in this case introducing of manganese leads to the simple substitution of the vacancies in the cation sublattice. Thus, if decreasing electrical conductivity caused by decreasing mobility of the carriers, increasing of the thermoelectric *Q*-factor is associated with a change of a power spectrum of the valence states at the expense of increasing hole mass.

### *3.2. Solid solutions SnTe - $Cu_2Te$ (B)*

The interaction of the basic matrix with the copper telluride can occur in two ways: first, to retain stoichiometry on metal, or second, to retain that on tellurium.

$$\begin{aligned}&1)\ 1/2\mathrm{Cu}^{+}_{2}\mathrm{Te}^{2-}\rightarrow\mathrm{Cu}^{+}\mathrm{Te}^{2-}_{0,5}\\&V''_{\mathrm{Sn}}V^{\cdot\cdot}_{\mathrm{Te}}+\mathrm{Cu}^{+}\mathrm{Te}^{2-}_{0,5}\rightarrow\mathrm{Cu}'_{\mathrm{Sn}}(\mathrm{Te}^{\times}_{0,5}V^{\cdot\cdot}_{0,5})_{\mathrm{Te}}\\&(1-\beta)\mathrm{Sn}^{\times}_{\mathrm{Sn}}\mathrm{Te}^{\times}_{\mathrm{Te}}+\beta(\mathrm{Cu}'_{\mathrm{Sn}}(\mathrm{Te}^{\times}_{0,5}V^{\cdot\cdot}_{0,5})_{\mathrm{Te}})\rightarrow\\&\rightarrow(\mathrm{Sn}^{\times}_{1-\beta}\mathrm{Cu}'_{\beta})_{\mathrm{Sn}}(\mathrm{Te}^{\times}_{1-0,5\beta}V^{\cdot\cdot}_{0,5\beta})_{\mathrm{Te}}\rightarrow\\&\rightarrow(\mathrm{Sn}^{\times}_{1-\beta}\mathrm{Cu}^{\times}_{\beta})_{Sn}(\mathrm{Te}^{\times}_{1-0,5\beta}V^{\cdot\cdot}_{0,5\beta})_{\mathrm{Te}}+\beta e'\end{aligned}\tag{3}$$

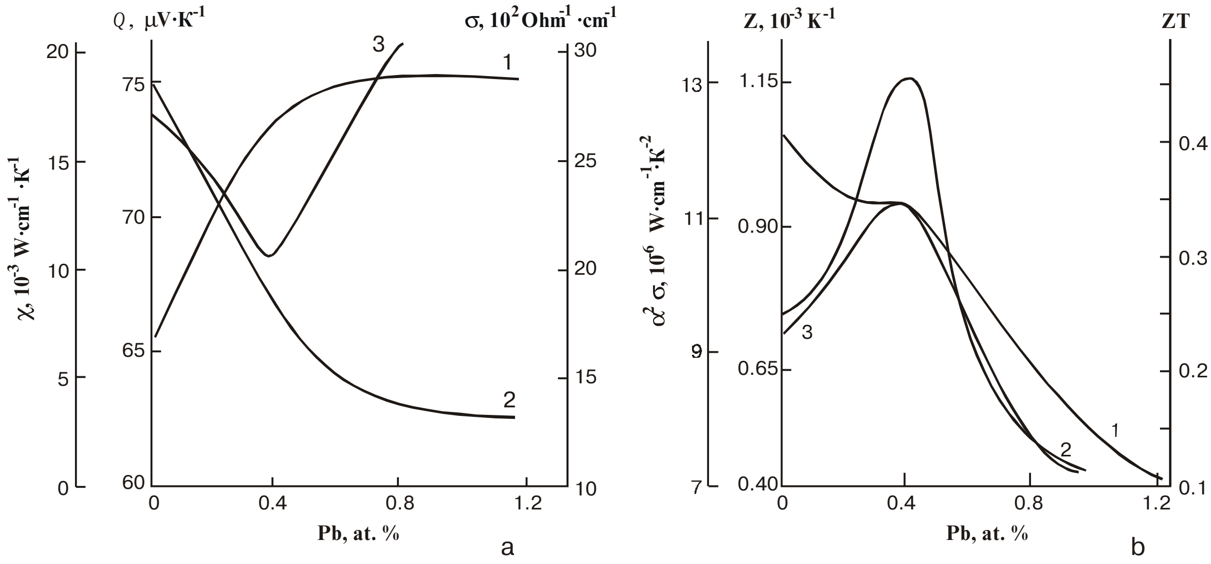

**Fig. 3.** Thermoelectric properties of the SnTe-$In_2Te_3$ alloy versus concentration of lead impurity at 300 K:
a – thermoelectric Q-factor ($\alpha$ – 1), electroconductivity ($\sigma$ – 2), lattice thermal conductivity ($\chi$ – 3);
b – thermoelectric power ($\alpha^2\sigma$ – 1), thermoelectric quality (Z – 2), dimensionless thermoelectric quality (ZT – 3).

$$\begin{gathered}
2)\ V''_{\mathrm{Sn}}V^{\cdot\cdot}_{\mathrm{Te}}+\mathrm{Cu}_2^{+}\mathrm{Te}^{2-}\to \mathrm{Cu}'_{\mathrm{Sn}}(\mathrm{Cu}^{\cdot})_i\,\mathrm{Te}^{\times}_{\mathrm{Te}}\\
(1-\gamma)\mathrm{Sn}^{\times}_{\mathrm{Sn}}\mathrm{Te}^{\times}_{\mathrm{Te}}+\gamma(\mathrm{Cu}'_{\mathrm{Sn}}(\mathrm{Cu}^{\cdot})_i\,\mathrm{Te}^{\times}_{\mathrm{Te}})\to\\
\to(\mathrm{Sn}^{\times}_{1-\gamma}\mathrm{Cu}'_{\gamma})_{Sn}(\mathrm{Cu}^{\cdot}_{\gamma})\mathrm{Te}^{\times}_{\mathrm{Te}}\to\\
\to(\mathrm{Sn}^{\times}_{1-\gamma}\mathrm{Cu}^{\times}_{\gamma})_{Sn}(\mathrm{Cu}^{\cdot}_{\gamma})\mathrm{Te}^{\times}_{\mathrm{Te}}+\gamma e'
\end{gathered}\tag{4}$$

As seen, in this case, two versions of defective state creation are possible: the substitution of tin vacancies with the copper atoms and formation of anion vacancies or the same substitution in the cation sublattice and interstitials of copper. Thus, in any way, intensification of *n*-type conduction takes place. It is necessary point that with $x = 0.03$ the substitution processes dominates, and consequently they can be examined as tin telluride with different concentration of carriers. At $x > 0.03$ the formed compositions are solid solutions based on SnTe.

### 3.3. Solid solutions SnTe - In$_2$Te$_3$ (C)

At preservation the stoichiometry on the indium the solid-solution formation leads to the substitution of tin vacancies by indium and formation of the interstitial tellurium atoms:

$$\begin{gathered}
1/2\mathrm{In}_2^{3+}\mathrm{Te}_3^{2-}\to\mathrm{In}^{3+}\mathrm{Te}^{2-}_{3/2}\\
V''_{\mathrm{Sn}}V^{\cdot\cdot}_{\mathrm{Te}}+\mathrm{In}^{3+}\mathrm{Te}^{2-}(\mathrm{Te}^{2-}_{0,5})_i\to\mathrm{In}^{\cdot}_{\mathrm{Sn}}\mathrm{Te}^{\times}_{\mathrm{Te}}(\mathrm{Te}''_{0,5})_i\\
(1-\delta)\mathrm{Sn}^{\times}_{\mathrm{Sn}}\mathrm{Te}^{\times}_{\mathrm{Te}}+\delta(\mathrm{In}^{\cdot}_{\mathrm{Sn}}\mathrm{Te}^{\times}_{\mathrm{Te}}(\mathrm{Te}''_{0,5})_i\to\\
\to(\mathrm{Sn}^{\times}_{1-\delta}\mathrm{In}^{\cdot}_{\delta})_{\mathrm{Sn}}\mathrm{Te}^{\times}_{\mathrm{Te}}(\mathrm{Te}''_{0,5\delta})_i\to\\
\to(\mathrm{Sn}^{\times}_{1-\delta}\mathrm{In}^{\times}_{\delta})_{\mathrm{Sn}}\mathrm{Te}^{\times}_{\mathrm{Te}}(\mathrm{Te}''_{0,5\delta})_i+\delta h^{\cdot}
\end{gathered}\tag{5}$$

At preservation stoichiometry on tellurium, except for a substitution of tin vacancies by indium, formation of the padding cation vacancies takes place:

$$\begin{gathered}
1/3\mathrm{In}_2^{3+}\mathrm{Te}_3^{2-}\to\mathrm{In}^{3+}_{2/3}\mathrm{Te}^{2-}\\
V''_{\mathrm{Sn}}V^{\cdot\cdot}_{\mathrm{Te}}+\mathrm{In}^{3+}_{2/3}\mathrm{Te}^{2-}\to(\mathrm{In}^{\cdot}_{2/3}V''_{1/3})_{\mathrm{Sn}}\mathrm{Te}^{\times}_{\mathrm{Te}}\\
(1-\eta)\mathrm{Sn}^{\times}_{\mathrm{Sn}}\mathrm{Te}^{\times}_{\mathrm{Te}}+\eta((\mathrm{In}^{\cdot}_{2/3}V''_{1/3})_{\mathrm{Sn}}\mathrm{Te}^{\times}_{\mathrm{Te}})\to\\
\to(\mathrm{Sn}^{\times}_{1-\eta}\mathrm{In}^{\cdot}_{2\eta/3}V''_{1\eta/3})_{\mathrm{Sn}}\mathrm{Te}^{\times}_{\mathrm{Te}}\to\\
\to(\mathrm{Sn}^{\times}_{1-\eta}\mathrm{In}^{\times}_{2\eta/3}V''_{1\eta/3})_{\mathrm{Sn}}\mathrm{Te}^{\times}_{\mathrm{Te}}+\tfrac{2}{3}\eta h^{\cdot}
\end{gathered}\tag{6}$$

It is pointed that the interstitials of tellurium atoms are unlikely, because invoke useful increasing of an elastic energy of the crystal. Here, it is also necessary to mean that at localization of an impurity indium atoms in the cation sites, SnTe represents interaction of the defects of two types: the vacancies, that are in lattice owing to deviations from the stoichiometry and impurity defects with formation of complexes, in which these defects are both space-mated , owing to the new defect – the impurity atom of the substitution.

The padding doping of the composite complex (6) by lead predetermines a substitution of tin vacancies in the cation sublattice, which results in decreasing of hole concentration (decreasing of electrical conductivity and increasing of the thermoelectric *Q*-factor) (the Fig. 3a), as it can be described by the next crystaloquasichemical equation:

$$\begin{gathered}
(1-y)((\mathrm{Sn}^{\times}_{1-\eta}\mathrm{In}^{\times}_{2\eta/3}V''_{1\eta/3})_{\mathrm{Sn}}\mathrm{Te}^{\times}_{\mathrm{Te}}+\tfrac{2}{3}\eta h^{\cdot})+\\
+y(\mathrm{Pb}''_{\mathrm{Sn}}V^{\cdot\cdot}_{\mathrm{Te}})\to\\
(\mathrm{Sn}^{\times}_{(1-\eta)(1-y)}\mathrm{In}^{\times}_{2\eta/3(1-y)}\mathrm{Pb}^{\times}_{y}V''_{\eta/3(1-y)})_{\mathrm{Sn}}\times\\
\times(\mathrm{Te}^{\times}_{(1-y)}V^{\cdot\cdot}_{y})_{\mathrm{Te}}+\tfrac{2}{3}\eta(1-y)h^{\cdot}+2ye'
\end{gathered}\tag{7}$$

Confrontation of the maximum values of the thermoelectric *Q*-factor for the solid solutions SnTe – 10 mol.% MnTe ($0.35\times10^{-3}$K$^{-1}$), (Fig. 1b), SnTe – 3 mol.% Cu$_2$Te ($0.45\times10^{-3}$K$^{-1}$), (Fig. 2b), SnTe-In$_2$Te$_3$:0.4 at.% Pb ($0.9\times10^{-3}$K$^{-1}$), (Fig. 3b), shows that the composite doping of tin telluride (In$_2$Te$_3$ and Pb) leads to effective improvements of its thermoelectric characteristics.

## Conclusion

It is shown that the solid solutions SnTe-MnTe, SnTe-Cu$_2$Te and SnTe-In$_2$Te$_3$:Pb are characterized by improved thermoelectric parameters in matching with tin telluride at the expense of decreasing of the thermal conductivity factor. The maximum value of the thermoelectric *Q*-factor takes place in SnTe-In$_2$Te$_3$:0.4 at.%Pb. Formation of the solid solutions leads: to substitution of tin vacancies of the basic matrix (SnTe-MnTe); substitution of the tin vacancies and formation of an anionic vacancies or copper interstitials (SnTe-Cu$_2$Te); substitution of the tin vacancies and formation of padding cation vacancies (SnTe-In$_2$Te$_3$).

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