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EFFECTS OF Pb DOPING ON THE SEEBECK CO-EFFICIENT AND ELECTRICAL PROPERTIES OF $Tl_{8.67}Pb_xSb_{1.33-x}Te_6$ CHALCOGENIDE SYSTEM

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We present the effects of Pb doping on the electrical and thermoelectric properties of Tellurium Telluride $Tl_{8.67}Pb_xSb_{1.33-x}Te_6$ (x=0.61, 0.63, 0.65, 0.67, 0.68, 0.70), prepared by solid state reactions in an evacuated sealed silica tubes. Additionally crystal structure data were used to model the data and support the findings. Structurally, all these compounds were found to be phase pure as confirmed by the x-rays diffractometery (XRD) and energy dispersive x-rays spectroscopy (EDS) analysis. The Seebeck co-efficient (thermopower) (*S*) was measured for all these compounds which show that *S* increases with increasing temperature from 295 to 550 K. The Seebeck coefficient is positive for the whole temperature range, showing p-type semiconductor characteristics. Complex behavior of Seebeck coefficient for Pb doped compounds has been observed that at room temperature, the values of S for *Pb* based compounds have complex behavior, first S decreasing with increase in *Pb* concentration i.e. x=0.65, and then S increases with increase in *Pb* contents upto x=0.70. Similarly the electrical conductivity (σ) and the power factors have also complex behavior with *Pb* concentrations. The power factor ($PF=S^2\sigma$) observed for $Tl_{8.67}Pb_xSb_{1.33-x}Te_6$ compounds are increases with increase in the whole temperature range (290 K-550 K) studied here. Telluride's are narrow band-gap semiconductors, with all elements in common oxidation states, according to $(Tl^+)_9(Sb^{3+})(Te^{2-})_6$. Phases range were investigated and determined with different concentration of *Pb* with consequents effects on electrical and thermal properties.

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Seebeck co-efficient, Electrical conductivity, Effects on power factor

1. Introduction

Thermoelectrics (TE's), as one of the most promising approaches for solid-state energy conversion between heat and electricity, is becoming increasingly important within the last decade as the availability and negative impact of fossil fuels draw increasing attention. Various TE's materials with a wide working temperature range (from 10 to 1000 K) for different applications in cooling and power generation have been extensively studied [1-5]. Tellurium telluride ((Tl_5Te_3)) is one of the most studied and used intermediate temperature TE materials with good thermoelectric properties , suitable for power generation applications such as waste heat recovery [1] and potentially in solar energy conversion [2]. Tellurium telluride based alloys are very attractive thermoelectric (TE) materials due to their high energy conversion efficiency at ambient temperature without requiring any driving parts or cooling system in electronic devices [3-7].

The dimensionless figure of merit, $ZT=S^2\sigma T/\kappa$, where σ is the electrical conductivity, κ is the thermal conductivity, *S* is the Seebeck coefficient, and *T* is the absolute temperature determine the effectiveness of a material for thermoelectric applications [8]. The thermal and electrical properties are determined by the power factor, defined as $S^2\sigma$. The power factor can be optimized as a function of the carrier concentration; with the help of different doping concentration and injections of free electrons in the chalcogenide system.

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We have explored chalcogenide with lead doped tellurium telluride materials with more complex compositions and structures which is likely to have more complex electronic structures. The materials which are most suitable and feasible for thermoelectric applications require the decoupling of an unusual combination of electrical and thermal behavior. The challenge lies in achieving simultaneously high electrical conductivity σ, high Seebeck co-efficient S, and low thermal conductivity k. These properties can be controlled by the electronic structure of the system, i.e. band gap, band shape, and band degeneracy near the Fermi level, electronic concentrations, and scattering of charge carriers (electrons or holes) which are strongly depends on each other [7-8].

Attempts from the last three decades to improve thermoelectric efficiency of different system have met with very limited achievements, the system of Bi_2Te, and $Tl_{10}SbTe_6$ remains the best thermoelectric materials for room and mid-temperature operation [9]. As mentioned by different researchers, traditionally, high ZT values are observed in moderate to heavily doped semi-conductors system [8]. In semiconductors, the thermal conductivity is dominated by the lattice component thus the problem of producing a high ZT value reduces to maximising the power factor $S^2 \sigma$ and minimizing κ_L[7-10]. The power factor depends significantly on details of the electronic band structure and carrier scattering mechanism. For obtaining large power factor we have to maximize the Seebeck co-efficient and the electrical conductivity ($S^2 \sigma$). For most of the thermoelectric systems the Seebeck co-efficient and electrical conductivity are mutually irreconcilable. The high power factor can be achieved in chalcogenide system, with high degree of degeneracy with several co-existing bonding types having complex band structure, and different scattering mechanism. The chalcogenide system which satisfies the above mentioned requirements are the *Pb* doped system of $Tl_{8.67}Sb_{1.33}Te_6$. There is a few studies on the on the thermoelectric properties of *Pb* doped $Tl_{8.67}Sb_{1.33}Te_6$ compound. Structural, electrical and thermoelectric properties of these compounds have been studied over temperature rang 300 to 550 K as a function of deviation from stoichiometry.

Heavy metals doped semi-conductors materials are considered most efficient thermoelectric system as due to their electronic structure calculations. To optimize the thermal and electrical properties, the chalcogenide system will doped to get optimized charge carrier concentrations of the order of 10^{19}-10^{21} carriers per cubic centimeter [10-12]. As studied before [13-15], heavy elements are known to contribute to low thermal conductivity an important asset of enhanced thermoelectric properties. This particularly appears to be true for materials containing thallium. Various thallium chalcogenides bestow with an extremely low lattice thermal conductivity with values significantly below 1 W/mK, likely a consequence of the high mass of thallium and its tendency to complex low symmetry coordination spheres [16]. The crystal structure type adopted by $Tl_9Sb_1Te_6$ is an ordered variant of Tl_5Te_3, space group I4/mcm.

The main objective of this research work is to study and optimize the temperature dependence of the electrical and thermal features of *Pb* doped Tellurium Telluride $Tl_{8.67}Pb_xSb_{1.33-x}Te_6$ over a large temperature span and to see the potential of these materials for the thermoelectric applications, e.g. thermoelectric power generator. To develop high-performance bulk thermoelectric materials, we investigated thallium compounds as these types of materials have extremely low thermal conductivity as well as moderate electrical performance [**17**]. We have investigated the properties of $Tl_{8.67}Pb_xSb_{1.33-x}Te_6$ compound due to their low thermal conductivity and high electrical conductivity and potential for their use as high performance bulk thermoelectric materials.

2. Experimental

The *Pb* doped $Tl_{8.67}Pb_xSb_{1.33-x}Te_6$ (x=0.61, 0.63, 0.65, 0.67, 0.68, 0.70) has been prepared by solid state reactions in evacuated sealed silica tubes. The purpose of this study were mainly for discovering new type of ternary and quaternary compounds by using Tl^{+1}, Pb^{+2}, Sn^{+3}, Sb^{+3} and Te^{-2} elements as the starting materials. Direct synthesis of stoichiometric amount of high purity elements i.e. 99.99 % of different compositions have been prepared for a preliminary investigation. Since most of these starting materials for solid state reactions are sensitive to oxygen and moistures, they were weighing stoichiometric reactants and transferring to the silica tubes in the glove box which is filled with Argon and then were sealed in a quartz tube. Before putting these samples in the resistance furnace for the heating, the silica tubes was put in vacuum line to evacuate the argon and then sealed it. This sealed powder were heated up to 650 C^o at a rate of 1 k/min and kept at it for 24 hours. The sample was cooled down with extremely slow rate to avoid quenching, dislocations, and crystals deformation. The Heating profile for these compounds is: room temperature (RT)-12 h-650 C-24 h-650 C-60 h-560 C-70 h-400C-RT.

Structural analysis of all these samples was carried out by x-rays diffraction, using an Inel powder diffractometer with position-sensitive detector and CuKα source at room temperature. All the peaks observed in the XRD data are indexed with the reported, and no impurities were observed in any of the studied sample. X-ray powder diffraction patterns confirm the single phase composition of the compounds.

The temperature dependence of Seebeck co-efficient was measured for all these compounds on a cold pressed pellet in rectangular shape, of approximately 5x1x1 mm^3 dimensions. The air sensitivity of theses samples was checked (for one sample) by measuring the thermoelectric power and confirmed that these samples are not sensitive to air. This sample exposes to air more than a week, but no appreciable changes observed in the Seebeck values. The pellet for these measurements was annealed at 400 C for 6 hours.

For the electrical transport measurements 4-probe resistivity method was used and the pellets were cut into rectangular shape with approximate dimension of 5x1x1 mm.

3. Results and discussions

3.1. Structural analysis

Various concentrations of *Pb* doped $Tl_{8.67}Pb_xSb_{1.33-x}Te_6$ compounds series were synthesized, and their physical properties were studied for x=0.61, 0.63, 0.65, 0.67, 0.68, 0.70. The powder x-rays diffraction pattern which is measured at room temperature for all these compounds is presented in Fig. 1. It is found that the tetragonal single phase $Tl_9Sb_1Te_6$ is obtained in the present study. The tetragonal lattice parameters observed at room temperature are a = 0.866 nm and c= 1.305 nm, in well agreement with the literature data [18]. The materials are isostructural with the binary tellurium telluride $Tl_{10}Te_6$, and the crystal structure of $Tl_9Sb_1Te_6$ was determined with the experimental formula, possessing the same space group 14/mcm as Tl_5Te_3 and $Tl_8Sb_2Te_6$, in contrast to $Tl_9Sb_1Te_6$ that adopt the space group 14/m. The energy dispersive x-rays spectroscopy was used to confirm the elemental and compositional analysis as expected in the sample. EDX data for $Tl_{8.67}Pb_{0.63}Sb_{0.70}Te_6$, collected at room temperature are shown in Fig. 2, conformed the elemental and compositional analysis in the Pb doped chalcogenide system, with all other compounds have the same stoichiometric ratio as designed.

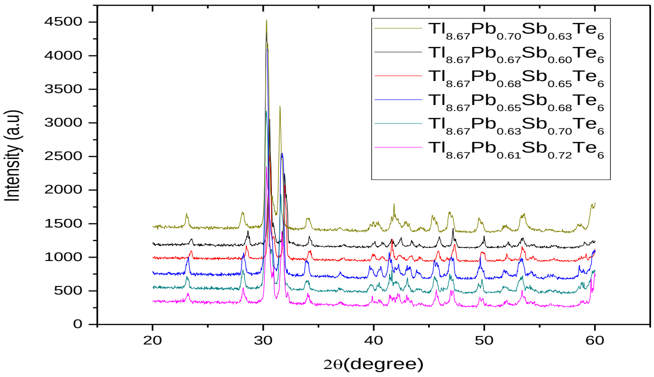
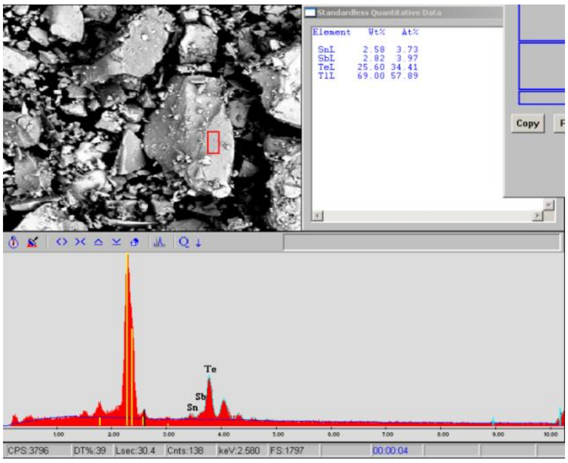


Fig. 1. XRD data of $Tl_{8.67}Pb_xSb_{1.33-x}Te_6$ (x=0.61, 0.63, 0.65, 0.67, 0.68, 0.70), collected at room temperature.



Standardless Quantitative Data

Element	Wt%	At%
SnL	2.58	3.73
SbL	2.82	3.97
TeL	25.60	34.41
TlL	69.00	57.89

Fig. 2. EDX data for $Tl_{8.67}Pb_{0.63}Sb_{0.70}Te_6$, collected at room temperature are shown here, to conform the elemental analysis in the system, with all other compounds have the same stoichiometric ratio as designed.

3.2. Physical properties

We have studied the effect of reduction of the charge carriers in thermal and transport characteristics *Pb* content was increased in $Tl_{8.67}Pb_xSb_{1.33-x}Te_6$ by replacing *Sb* atoms according to the formula. The temperature variation as a function of the Seebeck coefficient (S) for the $Tl_{8.67}Pb_xSb_{1.33-x}Te_6$ (x=0.61, 0.63, 0.65, 0.67, 0.68, 0.70) compounds are shown in Fig. 3. The Seebeck coefficient was measured in the temperature gradient of 1 K. The positive Seebeck co-efficient increases smoothly with increasing temperature from 300 K to 500 K, for all compounds in particularly for p-type semiconductors having high charge carrier concentration. It is apparent that this chalcogenide system exhibit positive thermopower for the whole temperature range, signifying that the p-type (hole) carriers conduction dominates the thermoelectric transport in these compounds. When the amount of Pb increased from 0.61 to 0.65, the effect of increasing hole concentration, decreases that of the electron scattering, resulting in the reduction of thermopower. On the other hand when the amount of *Pb* doping is larger than 0.65 (as *x* increased further), the *Pb* doping will increase the carrier's density. However, the smaller grains upon *Pb* doping are responsible for the enhancement of electron scattering, yielding an increase of the thermopower and effective mass in the chalcogenide system [19-20]. It is observed in our study that only an optimum concentration of *Pb* could enhance the Seebeck coefficient in this particular system. In other words the Seebeck coefficient will decrease suddenly on doping from the optimum value of *Pb* concentration in this compound. Improvements could be achieved by optimizing the dopants (Pb here) and their concentration to simultaneously improve the charge mobility which will be responsible for the enhancement of Seebeck coefficient [21] in this system.

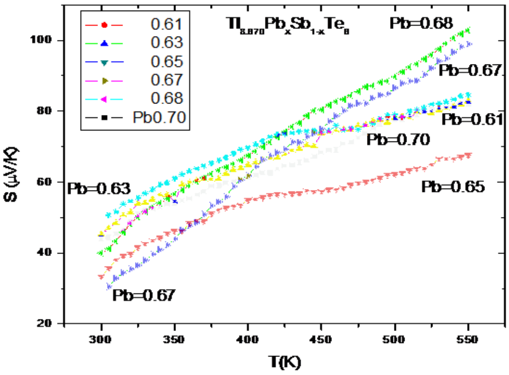


Fig. 3.Temperature dependence of Seebeck Co-efficient of $Tl_{8.67}Pb_xSb_{1.33-x}Te_6$ (x=0.61, 0.63, 0.65, 0.67, 0.68, 0.70).

The Seebeck coefficient varies from 80 to 130 $\mu V/K$ as a function of temperature. Here the increasing behavior of Seebeck co-efficient is due to that of lowering Fermi energy level caused by decreasing carrier density [22]. In low doping concentration the smallest number of charge carriers and large number of holes is observed in our system which results the highest value of thermopower, as shown in Fig.4. In large x i.e. higher *Pb* contents occurs with higher numbers of electrons and thus few charge carriers.

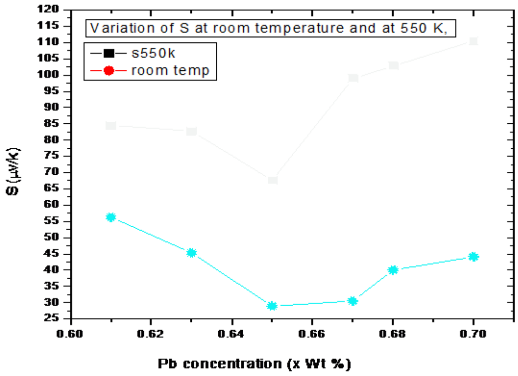


Fig. 4. Seebeck co-efficient dependence on x (x=0.61, 0.63, 0.65, 0.67, 0.68, 0.70) are shown for $Tl_{8.67}Pb_xSb_{1.33-x}Te_6$ at 305 and 550 K.

The temperature variations of electrical conductivity of the quaternary compounds are shown in Fig. 5.

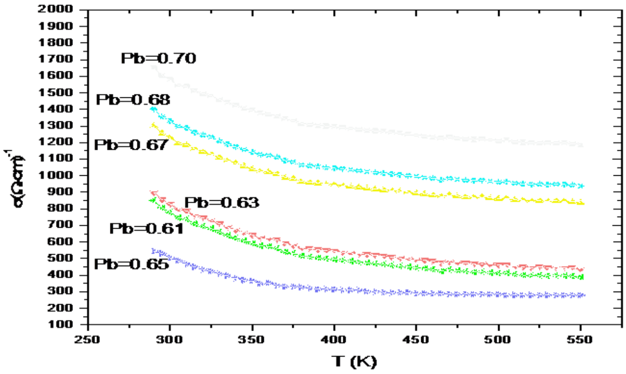


Fig. 5.Temperature dependence of conductivity of $Tl_{8.67}Pb_xSb_{1.33-x}Te_6$ (x=0.61, 0.63, 0.65, 0.67, 0.68, 0.70) of the cooled pressed pellet, with heating profile.

The electrical conductivity observed for all the samples studied here, decreases with increasing temperature, showing the degenerate semiconductor behavior due to positive temperature coefficient, resulting from the phonons scattering of charge carriers and grains boundaries effects [23]. An increasing the *Pb* concentration, which is to increase the number of holes in the compound, is what we have experimental observed. The minor temperature dependency may be caused by more grain boundary scattering. In this particular Pb doped chalcogenide system, we have observed no systematic trend in the variation of the electrical conductivity for the $Tl_{8.67}Pb_xSb_{1.33-x}Te_6$ with *Pb* concentration. The low electrical conductivity in the pressureless sintered chalcogenide system [23-26] may be caused by the oxide impurity phase in the grain boundary. The lead doping concentration and grain boundary mechanism are playing significant role for controlling the electrical conductivity in the chalcogenide system.

The band structure calculations for Tl_9SbTe_6 and $Tl_8Sn_2Te_6$ suggest that $Tl_8Sn_2Te_6$ is a heavily doped p-type semiconductor with a partially empty valence band, while the Fermi-level in

$Tl_8Sn_2Te_6$ is located in the band gap as reported [5]. With these observations, increasing lead concentration, lowering of thermal and electrical conductivity is observed in this particular chalcogenide system. For the Seebeck coefficient, we have observed an opposite trend; increasing *Pb* concentration, causes Seebeck values increases.

The temperature behavior as the doping concentration *x*, is varied, and can be relates it to Seebeck coefficient, temperature and injected charge carrier concentration displayed below [10]:

$$s = \frac{8\pi^2 k_B^2}{3eh^2} m^*.T(\frac{\pi}{3n})^{2/3}$$

Where, K_B, is the Boltzmann constant, *e* is the electronic charge, *h* is the Plank's constant, m^* is the effective mass, and *n* is the charge carrier concentration. The effective mass and carrier concentration are two parameters which affects the Seebeck coefficient. Hence the samples with lower concentration (small *x, and high n*), will shows linearly increasing thermopower with increase in temperature. Those with small *n* and large x, that increases with temperature, causes a decrease in the Seebeck coefficient, once the sufficient charge carriers are able to cross the band gap of the compound studied. Using E_{gap}=$2eS_{max}T_{max}$ [24], a gap of 0.23 eV has been calculated for $Tl_{8.67}Pb_{0.70}Sb_{0.63}Te_6$ system.

The electrical conductivity, σ, for the $Tl_{8.67}Pb_xSb_{1.33-x}Te_6$ compounds with $0.61 \leq x \leq 0.70$ as shown in Fig. 5, decreases with increase in temperature across the entire temperature range examined; these results are the indicative of metallic behavior, an evidence of a relatively high carrier concentration. Increased, doping concentration causes decrease in σ, as expected and inversely affecting their Seebeck counterpart. The $Tl_{8.67}Pb_{0.70}Sb_{0.60}Te_6$ displays the highest value of 1650 $(\Omega\text{-cm})^{-1}$ at 290 K, and $Tl_{8.67}Pb_{0.65}Sb_{0.65}Te_6$ displays the lowest with 545 $(\Omega\text{-cm})^{-1}$ and the samples with x= 0.61 and 0.63, almost have very close values of about 850 and 900 $(\Omega\text{-cm})^{-1}$ respectively. The conductivity differences at room temperature between the hot pressed pellet and the ingot was observed a little change from 850 to 855 $(\Omega\text{-cm})^{-1}$ respectively for the $Tl_{8.67}Pb_{0.63}Sb_{0.70}Te_6$ compound.

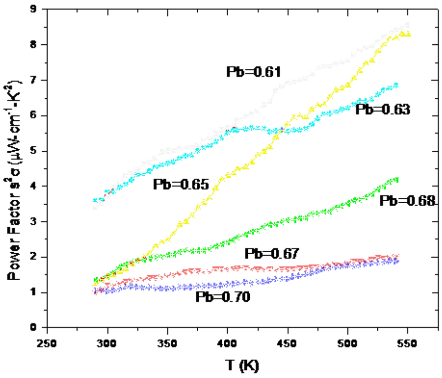


Fig. 6.Variation of Power factor with temperature and their dependency on doping concentration for $Tl_{8.67}Pb_xSb_{1.33-x}Te_6$ *(x=0.61, 0.63, 0.65, 0.67, 0.68, 0.70).*

To enhance the power factor (PF= S^2 σ) for these compounds, we need to decouple the electrical conductivity from the Seebeck co-efficient, usually inversely proportional to each other in these systems. The main contribution in the PF comes from the Seebeck co-efficient, so we have to design the materials such that their *S* should be enhanced. The power factors calculated from the electrical conductivity σ, and the Seebeck co-efficient S, obtained for these compounds are displayed in Fig. 6. The power factor increases with increasing temperature for all these compounds. The power factor shows very complex behavior with the doping of Pb concentrations. The $Tl_{8.67}Pb_{0.60}Sb_{0.70}Te_6$ compound display the highest value 8.56 $(\mu\text{Wtt-cm}^{-1}\text{-K}^{-2})$ of PF at 550 K and 3.52 56 $(\mu\text{Wtt-cm}^{-1}\text{-K}^{-2})$ at 290 K. The lowest PF factors were observed for $Tl_{8.67}Pb_{0.70}Sb_{0.60}Te_6$ compound which have values of 1.66 56 $(\mu\text{Wtt-cm}^{-1}\text{-K}^{-2})$ at 550 K and 1.01 56 (µWtt-cm^{-1}-K^{-2}) at 290 K. As discussed before, an increasing lead concentration , is expected to increase the number of holes. This trend is experimental observed: with increasing x, the Seebeck co-efficient decreases and then increases after optimized value of Pb concentration, which results in increase in the S. The minor temperature dependence $Tl_{8.67}Pb_{0.70}Sb_{0.60}Te_6$ compound is due to large number of grain boundary scattering.

4. Conclusions

Various concentrations of *Pb* doped $Tl_{8.67}Pb_xSb_{1.33-x}Te_6$ compounds series were synthesized, and their physical properties were studied for x=0.61, 0.63, 0.65, 0.67, 0.68, 0.70. These materials are single phase as confirmed by x-rays diffractometery and the crystal structure of $Tl_8Sb_2Te_6$ was determined with the experimental formula, possessing the same space group 14/mcm as Tl_5Te_3.

The thermoelectric properties of polycrystalline $Tl_{8.67}Pb_xSb_{1.33-x}Te_6$ compounds were measured in the temperature range from room temperature to about 550 K. The Seebeck coefficient is positive in the whole temperature range, and is increasing with increase in temperature, conferring that hole conduction dominates in these compounds. For higher concentrations of Pb, the Seebeck co-efficient of the doped tellurium telluride is decreasing due to increasing hole concentration which in turns increasing the electron scattering in this Pb doped chalcogenide system. On the other hand when the amount of Pb doping is more than 0.65, the Pb doping will increase the carrier’s density. However, the smaller grains upon Pb concentrations will enhance the electron scattering, resulting increase in thermopower. Further improvements appear to be possible by optimizing the materials on both the micro and nano level, as demonstrated for PbTe in different studies [5, 15, 26]. Moreover, different partial substitutions may optimize, or decrease the performance, with different dopants, which remains to be investigated. This is an investigation for the optimization of lead dopants concentration to achieve desirable thermoelectric properties and to optimize different physical properties in *Pb* doped $Tl_{8.67}Pb_xSb_{1.33-x}Te_6$ chalcogenide system.

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