SYNTHESIS AND CHARACTERIZATION OF CHALCOGENIDES BASED NANOMATERIALS FOR THERMOELECTRIC APPLICATIONS

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By

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Dedicated to my family and teachers

Certificate

This is to certify that the the thesis entitled "**Synthesis and Characterization of Chalcogenides Based Nanomaterials for Thermoelectric Applications**" being submitted by **Mr. Pradeep Kumar Sharma** to the **Department of Physics, Indian Institute of Technology Delhi**, for the award of degree of '**Doctor of Philosophy**' is a record of bonafide research work carried out by him under our supervision and guidance. He has fulfilled the requirements for the submission of this thesis, which in our opinion, has reached the requisite standard.

The results contained in this thesis have not been submitted, in part or whole, to any other University or Institute for the award of degree/diploma.

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Candidate's Declaration

This is to certify that the research work presented in the thesis entitled "**Synthesis and Characterization of Chalcogenides Based Nanomaterials for Thermoelectric Applications**" is an original contribution. This work has been carried outa at Thin Film Lab, Department of Physics, Indian Institute of Technology Delhi, and CSIR-NPL, New Delhi, for the award of degree of '**Doctor of Philosophy in Physics**'. This work presented in the thesis has not been submitted anywhere for the award of any degree, diploma, associateship, fellowship, or any other similar title of recognition.

I declare that I have devotedly acknowledged, given credit, and referred to the research workers whenever their works have been cited in the text and the body of the thesis. The extent of information derived from existing literature has been indicated in the body of the thesis at appropriate places giving the source of information.

Mr. Pradeep Kumar Sharma

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Dated:

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Mr. Pradeep Kumar Sharma

Dated:

Abstract (English)

With the world's increasing energy demands, concerns over climate change, and wastage of nearly two-third of energy in the form of heat, there is a compelling demand for clean energy sources and efficient energy conversion technologies. Thermoelectric energy (TE) conversion has emerged out as a potential technique to convert automotive and other industrial waste heat into useful electricity. The thermoelectric devices are silent, reliable, eco-friendly, and are devoid of any moving parts. Hence, this technology is considered as a future clean and sustainable energy source.

In the present work, a compact thermopower measurement set up, capable of carrying out the measurements in the mid-temperature range (300-700 K), has been designed, developed, and fabricated in-house. The set-up is calibrated first by measuring thermopower of Constantan, Alumel, and Chromel specimen (reference material) at 313 K. The two data sets obtained on the sample of $CaMnO_3$ in the temperature range of 300-700 K, using the presently developed set-up and a commercial set-up (M/s LINSIES, Model LSR 3), are in fair agreement.

Lead telluride (PbTe) is an excellent compound for power generation applications in the mid-temperature range (500-800 K) among all the metal chalcogenides due to its appropriate intrinsic properties *i.e.*, high Seebeck coefficient, high electrical conductivity, and low values of thermal conductivity. Hence, fabrication, fundamental understanding, and structure-material-property correlation of thermoelectric properties of the chalcogenides materials is a quite exciting area of investigation.

In the present work, a systematic investigation on structural and thermoelectric properties of Spark plasma sintered Lead telluride compound has been carried out.

The pristine lead telluride compound has been synthesized by hydrothermal route and a low temperature aqueous chemical route without using any organic solvent and surfactant. The thermoelectric properties of spark plasma sintered bulk nanostructured samples have been measured from RT to 700K. Notably, significant Seebeck coefficient and small electrical resistivity values are observed in the sample synthesized by the hydrothermal route, which is ascribed to the charge carrier energy filtering effect. A maximum reduction of∼38% and∼58% have been observed in the sample synthesized by the hydrothermal and aqueous chemical routes, respectively, compared to the bulk ingot. The maximum figure of merit attained is 0.18 at 673 K in the lead telluride sample synthesized by the hydrothermal route.

Controlled Bismuth doping at Pb Site successfully enhanced the electrical conductivity of PbTe-x % SiC nanocomposite samples by almost two orders of magnitude in comparison to pristine PbTe. The thermoelectric performance of the lead telluride compound has been further enhanced by doping with Bismuth at the Pb sites and incorporating 50 nm Silicon carbide nanoinclusions in the PbTe matrix. The incorporated SiC nanoinclusions offer significantly reduced thermal conductivity, which, combined with enhanced power factor, leads to a remarkably enhanced figure of merit. The zT_{max} value reaches 0.32 at 590 K.

Further, the effect of the presence of a two-dimensional (2D) Molybdenum Di-sulphide material on the electrical and thermal transport properties of PbTe-y% MoS_2 nanocomposite samples have been investigated in detail. Interestingly, the electrical conductivity of spark plasma sintered PbTe-MoS_2 nanocomposite samples decreases remarkably compared to the pristine PbTe sample. The incorporation of MoS_2 nanosheets in the PbTe matrix leads to an almost 38% reduction in thermal conductivity values (corrected for porosity). The combination of low thermal conductivity and moderate electrical conductivity values resulted in a zT_{max} value of 0.20 at 590 K.

Abstract (Hindi)

दुनिया की बढ़ती ऊर्जा मांगों के साथ, जलवायु परिवर्तन पर चिंता, और गर्मी के रूप में लगभग दो-तिहाई ऊर्जा की बर्बादी, स्वच्छ ऊर्जा स्रोतों और कुशल ऊर्जा रूपांतरण प्रौद्योगिकियों की जबरदस्त मांग है। थर्मोइलेक्ट्रिक ऊर्जा (टीई) रूपांतरण ऑटोमोटिव और अन्य औद्योगिक अपशिष्ट ताप को उपयोगी बिजली में परिवर्तित करने के लिए एक संभावित तकनीक के रूप में उभरा है। थर्मोइलेक्ट्रिक उपकरण मूक, विश्वसनीय, पर्यावरण के अनुकूल हैं, और किसी भी चलती भागों से रहित हैं। इसलिए, इस तकनीक को भविष्य के स्वच्छ और टिकाऊ ऊर्जा स्रोत के रूप में माना जाता है।

वर्तमान कार्य में, एक कॉम्पैक्ट थर्मोपावर माप स्थापित किया गया है, जो मध्य-तापमान रेंज (300-700 K) में माप करने में सक्षम है, को इन-हाउस डिज़ाइन, विकसित और गढ़ा गया है। सेट-अप को पहले 313 K पर कॉन्स्टेंटन, एल्यूमेल और क्रोमेल नमूने (संदर्भ सामग्री) के थर्मोपावर को मापकर कैलिब्रेट किया जाता है। वर्तमान में विकसित का उपयोग करके 300-700 K के तापमान रेंज में $CaMnO_3$ के नमूने पर प्राप्त दो डेटा सेट सेट-अप और एक वाणिज्यिक सेट-अप (मैसर्स LINSIES, मॉडल LSR 3), उचित समझौते में हैं।

लेड टेलुराइड (PbTe) अपने उपयुक्त आंतरिक गुणों यानी उच्च सीबेक गुणांक, उच्च विद्युत चालकता, और निम्न मूल्यों के कारण सभी धातु चाकोजेनाइड्स के बीच मध्य-तापमान रेंज (500-800 K) में बिजली उत्पादन अनुप्रयोगों के लिए एक उत्कृष्ट यौगिक है। ऊष्मीय चालकता। इसलिए, चाकोजेनाइड्स सामग्री के थर्मोइलेक्ट्रिक गुणों का निर्माण, मौलिक समझ और संरचना-सामग्री-संपत्ति सहसंबंध जांच का एक बहुत ही रोमांचक क्षेत्र है।

वर्तमान कार्य में, स्पार्क प्लाज़्मा सिंटर्ड लेड टेल्यूराइड यौगिक के संरचनात्मक और थर्मोइलेक्ट्रिक गुणों पर एक व्यवस्थित जांच की गई है। प्राचीन लेड टेलुराइड यौगिक को हाइड्रोथर्मल मार्ग और कम तापमान जलीय रासायनिक मार्ग द्वारा किसी भी कार्बनिक विलायक और सर्फेक्टेंट का उपयोग किए बिना संश्लेषित किया गया है। स्पार्क प्लाज़्मा सिंटर्ड

बल्क नैनोस्ट्रक्चर नमूनों के थर्मोइलेक्ट्रिक गुणों को RT से 700K तक मापा गया है। विशेष रूप से, महत्वपूर्ण सीबेक गुणांक और छोटे विद्युत प्रतिरोधकता मान हाइड्रोथर्मल मार्ग द्वारा संश्लेषित नमूने में देखे जाते हैं, जो चार्ज वाहक ऊर्जा फ़िल्टरिंग प्रभाव के लिए निर्दिष्ट है। थोक पिंड की तुलना में क्रमशः हाइड्रोथर्मल और जलीय रासायनिक मार्गों द्वारा संश्लेषित नमूने में 38% और ~58% की अधिकतम कमी देखी गई है। हाइड्रोथर्मल मार्ग द्वारा संश्लेषित लेड टेल्यूराइड नमूने में प्राप्त योग्यता का अधिकतम आंकड़ा 673 K पर 0.18 है।

Pb साइट पर नियंत्रित बिस्मथ डोपिंग ने PbTe-x% SiC नैनोकम्पोजिट नमूनों की विद्युत चालकता को प्राचीन PbTe की तुलना में परिमाण के लगभग दो क्रमों से सफलतापूर्वक बढ़ाया। लेड टेल्यूराइड कंपाउंड के थर्मोइलेक्ट्रिक प्रदर्शन को Pb साइटों पर बिस्मथ के साथ डोपिंग करके और PbTe मैट्रिक्स में 50 एनएम सिलिकॉन कार्बाइड नैनोइनक्लूजन को शामिल करके और बढ़ाया गया है। शामिल किए गए SiC नैनोइनक्लूजन काफी कम तापीय चालकता प्रदान करते हैं, जो कि बढ़ी हुई शक्ति कारक के साथ संयुक्त रूप से योग्यता के उल्लेखनीय रूप से बढ़े हुए आंकड़े की ओर जाता है। zT_{max} का मान 590 K पर 0.32 तक पहुंच जाता है।

इसके अलावा, PbTe-y% MoS_2 नैनोकम्पोजिट नमूनों के विद्युत और थर्मल परिवहन गुणों पर दो-आयामी (2D) मोलिब्डेनम डि-सल्फाइड सामग्री की उपस्थिति के प्रभाव की विस्तार से जांच की गई है। दिलचस्प बात यह है कि स्पार्क प्लाज्मा की विद्युत चालकता PbTe-MoS_2 नैनोकम्पोजिट नमूनों को प्राचीन PbTe नमूने की तुलना में उल्लेखनीय रूप से कम कर देती है। PbTe मैट्रिक्स में MoS_2 नैनोशीट को शामिल करने से तापीय चालकता मूल्यों (छिद्र के लिए सही) में लगभग 38% की कमी आती है। कम तापीय चालकता और मध्यम विद्युत चालकता मूल्यों के संयोजन के परिणामस्वरूप 590 K पर 0.20 का zT_{max} मान प्राप्त हुआ

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NOMENCLATURE

Symbols	
ΔV	Potential Difference
ΔT	Temperature Difference
S	Seebeck Coefficient
Q	Heat absorbed/liberated
Π	Peltier Coefficient
I	Electric current
T	Absolute Temperature
η	Thermoelectric conversion efficiency
T_H	Temperature of Hot Junctions
T_C	Temperature of Cold Junction
zT	Dimensionless Figure of Merit
$\boldsymbol{\sigma}$	Electrical Conductivity
$\boldsymbol{\kappa}$	Thermal Conductivity
$\boldsymbol{\kappa}_e$	Electronic Thermal Conductivity
$\boldsymbol{\kappa}_l$	Lattice Thermal Conductivity
$\boldsymbol{\kappa}_{Bipolar}$	Bipolar Thermal Conductivity
n/p	Electron/Hole Carrier Density
e	Electronic Charge
μ	Charge Carrier Mobility
k	Boltzmann Constant
h	Planck Constant
L	Lorentz Number

$S^2\boldsymbol{\sigma}$	Power Factor
R_H	Hall Coefficient
d	Thermal Diffusivity
C_p	Specific Heat Capacity
m*	Charge Carrier Effective Mass
H_v	Vickers Pyramid Number
N_v	Orbital Degeneracy
E	Energy
E_F	Fermi Energy
θ_D	Debye Temperature
E_B	Depth of Potential Barrier

ABBREVATIONS

Symbols	
TE	Thermoelectric
DOS	Density of States
PGEC	Phonon Glass Electron Crystal
XRD	X-ray Diffraction
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
HR-TEM	High Resolution Transmission Electron Microscopy
DSC	Differential Scanning Calorimetry
JCPDS	Joint Committee on Powder Diffraction Standards
STEM	Scanning Transmission Electron Microscopy
HAADF	High-angle annular dark-field scanning transmission electron microscopy
ABF-STEM	Annular bright-field scanning transmission electron microscopy